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FOREWORD

The policy of the Board of Directors has been to segregate the publications of the American Institute of Mining and Metallurgical Engineers into groups that deal with a single one of the minerals or with some single general aspect of mining or metallurgy. The first volumes of this kind were discussions of the nature and origin of ore deposits, and these were followed later by a volume containing a remarkable series of papers on mining in Montana, volumes on pyrometry, mining methods, and others that were issued as volumes of the TRANSACTIONS series, or closely similar.

Meanwhile it had become evident that progressive specialization in the mining industry had advanced to the point where there was not only needless waste in supplying all our members with all the papers on all subjects presented before the institute, but it was even disadvantageous, because it is less easy to consult the papers on a given topic if they are included with many others in a single volume. A beginning was therefore made by publishing all the papers dealing with petroleum in a single annual volume, "Petroleum Development and Technology," which is sent automatically to all who have indicated their desire to receive it, but to others only on request.

This proving satisfactory, a second series was started by the publication in an annual separate volume of all the papers presented before the Institute of Metals Division meetings. The present volume is the first of a similar series to include all papers dealing with iron and steel. As in the case of the others it will be sent regularly to those who have registered for the publications on these subjects, but to others only on request. It is therefore essential that everyone who wishes to receive all the iron and steel papers as published should register as a member of the Divison.

The iron and steel activities of the Institute have been a most important phase of its work since it was first organized in 1871, in fact the early volumes, in some cases, were largely devoted to that subject and much of the best material dealing with the development of iron and steel technology in America is to be found in the early volumes of the TRANSACTIONS. Until last year the activities of this group were directed by an Iron and Steel Committee with some sixty or more members, which in recent years followed the custom of holding a luncheon meeting in February of each year and a dinner meeting in May and October.

FOREWORD

At its meeting on Feb. 20, 1928, this committee voted to request the Board of Directors to authorize it to organize as an Iron and Steel Division. The required authorization being granted, the Committee at its next meeting, on May 28, 1928, duly organized as a Division, and adopted a set of "Rules and Regulations" (which was published on pages 318-319 of MINING AND METALLURGY for July, 1928) which provide that any member of the Institute may become a member of the Division by signifying in writing the desire to do so. To date relatively few members of the Institute have formally expressed that desire but this volume will be sent to all members who have previously signified their desire to receive papers classed as "C-Iron and Steel." In the future the system will be adhered to of sending the publications of the Division regularly only to those who have registered as members of the Division, and to others only on request.

Most of the papers included in this volume were presented and discussed at the meeting in New York in February, 1928, when four sessions for the reading and discussion of papers were held. One paper, that by C. H. Mathewson and G. H. Edmunds, on "The Neumann Bands in Ferrite," was presented and discussed at the meeting in Philadelphia on Oct. 10, 1928.

This volume also includes the Henry M. Howe Memorial lecture, presented in 1928 by Henry D. Hibbard, his subject being "The Significance of the Simple Steel Analysis."

Current material of interest in regard to iron and steel is presented monthly in MINING AND METALLURGY, therefore to obtain a complete record of the activities of the Iron and Steel Division for the year reference should be made to that journal as well as to this volume.

H. FOSTER BAIN,
Secretary, A. I. M. E.

Significance of the Simple Steel Analysis

By HENRY D. HIBBARD,* PLAINFIELD, N. J.

(Henry Marion Howe Memorial Lecture†)

AT THE beginning of a Henry M. Howe lecture it seems fitting to refer to Howe's great contributions to steel metallurgy, and particularly to the literature thereof. Most of my predecessors in this role have been able, from their association with him, to give direct testimony as to his great services; but although connected with him for years in a business way, I am less familiar with what might be called his academic side, except as it is embodied in his utterances, written and oral. Howe was adept in his genial way in extracting information in any line which, at the time, was of interest to him.

In a technical lecture one expects as a rule new knowledge—something about recent advances relating to the subject. On this occasion, however, I will ask you to go back with me to the primary department of steel lore, as the title of my lecture shows, to review the more fundamental features in that field for the purpose of seeking some gaps which we can fill and so give the subject renewed interest. In thus going back one must inevitably repeat many familiar facts, but that seems to be necessary in order to reach a clear understanding of the unrecorded matters.

The full interpretation of a steel analysis is at present unattainable, though much progress toward that end has been made. The ultimate analysis, giving the percentages of the five commonly determined elements, does indeed usually give a fair idea of what the steel is, and is ordinarily enough, with knowledge of its history and physical condition, to enable it to be assigned to some purpose or use for which it is reasonably suitable. But discrepancies arise.

Every maker and every user of steel knows, from at least occasional examples in his own experience, that the ultimate analysis is insufficient by itself to enable one to tell positively, from its interpretation, either the mechanical properties of the steel or its adaptability to the purpose for which it was made. Further, if, while having the specified composition, it is abnormal or unsatisfactory, why it is so. Good, bad and indifferent steels may have substantially the same ultimate analysis.

* Consulting Engineer.

† Presented at New York meeting, February, 1928.

The inconsistency of being better than expected, which means higher tensility or ductility or endurance in resisting shock or fatigue, some or all, comes as a rule from exceptional purity or freedom from harmful, or poisonous non-ferrous but undetermined ingredients. The inconsistency of being worse than the composition seemingly warrants may be due to one or more of a great number of physical and chemical causes which are included among the ills of steel. Some of these matters we are now to consider.

The crucible-steel maker of the last century exclaimed, "If you put the devil in the pot, the devil will come out of it." He had some justification for his opinion, as practically no oxidation or purification took place in the crucible, and the quality of the product depended chiefly on the purity of the melting stock used. Now, what is put into a steel charge, particularly in a basic furnace, while it must be suitable within limits, determines only in part what it is to be, and what service it is suitable for.

The commonest case of change in properties without change in composition is, of course, that of the ingot and the bar rolled therefrom. Heating and hot working improve the mechanical properties of practically all steels without appreciably changing the ultimate analysis. Up to certain limits, the more the work, the greater the improvement.

On this occasion we will limit our attention to plain or simple untreated steels and chiefly to those made by the open-hearth process. When bessemer, crucible or electric steels are referred to, the fact will be stated. Alloy steels, as well as heat-treated and cold-worked steels with their vast number of variations, must be reserved for the future. The upper limits of the five elements are taken to be: carbon, 1.5 per cent.; manganese, 1 per cent.; silicon, 0.6 per cent.; sulfur, 0.15 per cent.; phosphorus, 0.12 per cent.

VALUE OF ULTIMATE ANALYSIS

How far short the ultimate analysis may fall of telling the mechanical properties, a glance at Table 1 will show. This table gives approximately the maximum effects on tensility which may be and are effected by carbon, heat treatment and cold working, and shows the great extent of the field occupied even by simple steels. As a standard for comparison, Swedish wrought iron, considered as the purest iron obtainable, and having a tensility of 45,000 lb. per sq. in., is taken. The analysis is the same for all excepting the iron, but the variations in strength are exceedingly great.

By a full interpretation of an analysis is meant, among other things, that, given the composition, the mechanical properties could be told; that is, that chemical attributes would be convertible into physical.

TABLE 1.—*Extreme Increases in Tensility of Plain Steel Due to Carbon, Heat Treatment, and Cold Working in Pounds per Square Inch*
 In Each Case the Steel Has Been Hot-worked

Description	T. S.	Increases Due		
Iron (Swedish).....	45,000	To carbon	To heat treatment	To cold working
Iron plus 0.9 per cent. carbon.....	150,000	105,000		
Iron + 0.9 per cent. carbon + heat treatment.....	300,000	105,000	150,000	
Iron + 0.9 per cent. carbon + heat treatment + cold drawing.....	500,000	105,000	150,000	200,000

The tensility of 500,000 lb. per sq. in. is reached in small sizes of wire.

The converse of this is not true, of course, because various combinations of ingredients in different steels may give substantially the same physical or mechanical properties.

The differences existing between the properties of different pieces of steel of *good* quality, and of the same composition, are usually imparted by variations in the working and treatment they have undergone and only in a slight degree by variations in the undetermined impurities or ingredients.

In steels of *inferior* quality, on the other hand, while differences may be due also to working and treatment, they will be caused in a much greater degree by variations in the undetermined constituents.

An individual piece of steel may contain a flaw from which the next piece is free, but the matters that we have to consider are particularly those which relate to the metal itself and affect more or less all parts of the ingot.

So of two steels, perhaps from different sources, one may have better properties with inferior composition while the other has poorer properties with better composition in the common acceptation of the effects of the non-ferrous ingredients. For example, given two steels otherwise similar, the one with higher phosphorus content may be more ductile than the other with lower, just the opposite of what would be expected from the acknowledged effect of phosphorus in steel.

This statement of the inadequacy of the ultimate analysis is not confuted by the practice of using a formula to estimate some of the mechanical properties of some certain grade or kind of steel from its composition at some one steel plant where some particular variation of process is aimed to be followed, and the practice is, within limits, fairly regular; being, relatively speaking, more or less good. In such a case each element may be found to have an influence which is constant enough to be of some value in calculating the properties. But at some other works a different formula is required, and at any works a different

formula is demanded for acid steel from that applicable to basic. It is perhaps the undetermined constituents which chiefly interfere with the general use of some one formula.

Let us state some of the shortcomings of the ultimate analysis:

Shortcomings of the Ultimate Analysis

1. Such an analysis is incomplete. The undetermined constituents may be classified into harmless and harmful; conceding, of course, that they are present only in such proportions as actually exist in commercial plain steels.

The harmless undetermined ingredients include copper, arsenic, nickel, cobalt and aluminum, whose effects on the properties of plain steel are so small as to be of slight importance.

The harmful ingredients are the oxides, silicates and gases. Oxides are probably more prevalent in unfinished, and silicates in finished steel. The gases that injure quality are those which have formed holes in the metal. It seems likely that, in ordinary cases at least, gases in solution have little if any effect on the properties, but evidence on that point is incomplete. We do know, however, that steel may be killed, presumably by keeping its gases in solution, and have good physical and mechanical properties. The lack of a good practical method for determining oxygen in steel is commonly deplored.

2. For the elements which are determined an ultimate analysis is not enough, because, as we will see in Table 3, every one of the elements which enter into the composition of steel occurs at times in more than one state. Thus an element may be present as such, or may be alloyed with iron, or be combined with iron, or combined with some non-ferrous element or elements. Of course, no one element is or can be present in all of the four states. The ultimate analysis does not tell the numerous proximate ingredients formed by the elements in combination. To determine their compositions and amounts would be a substantial step forward, but only a step. In one state an element may have a beneficial and in another a harmful effect on the finished steel.

3. The ultimate analysis tells nothing of any elements, which have been contained or added, which have performed their beneficial service and in so doing have left the metal. A part or all of any silicon, aluminum, titanium, vanadium and manganese which may have been in the molten metal, either residual or added, may have so acted. When alloys have been added for such action the steel may be considered as being alloy-treated but still included in the category of simple or plain steels.

4. The manner in which the ingredients occur and are distributed in the metal is not told and on this its quality largely depends. Full

knowledge of the constitution of the steel must include this, for which end one employs the microscope rather than the beaker. Of internal defects which are not flaws such as welded gas holes, hard spots, collections of sonims and ghosts which more or less impair the mechanical attributes of a test piece in which they or some of them occur, the ultimate analysis gives no indication.

5. The part of the ingot from which the chemist's sample has been taken is often not known, especially when the analysis is made in the endeavor to find out why a certain abnormal steel is as it is, either notably good or notably bad.

A ladle sample properly taken represents the average of the heat well enough but if drillings for analysis are from a finished piece, the part of the ingot from which they came should be known, because of ghosts and regional segregation. If from a part rich in segregate, the figures obtained for carbon, sulfur and phosphorus will be higher than the average, and so mislead.

With enough silicon in the steel to kill it, say 0.25 per cent. or more, or some equally effective gas solvent, the constituent non-ferrous elements segregate but little, and the sample is likely to represent the average fairly well. But in steel partly killed or rimming, segregation is pronounced and the part of the ingot from which the drillings are taken should then be known. The larger the ingot, the more important this is. When less than one foot square, segregation is not as a rule important, and never so when the steel is killed.

6. The ultimate analysis gives no clue to the effects of improper casting temperature, which may be the direct cause of many shortcomings in the steel.

7. If the ultimate analysis were extended to meet all these shortcomings, so that one could know fully and exactly what was in the steel and how, a manifest impossibility, the evaluation or net effect of the whole on the properties might still be beyond us. Any mechanical defect occurring in steel may be due, of course, to causes in no way dependent on or connected with its composition.

Interpretation of Analyses Unsatisfactory

Inability to interpret analyses is an important reason why much that is written about steel is of little value to the steel maker. He reads of results obtained from and of properties possessed by some steel perhaps of a new kind, or for a new purpose, designated by its ultimate analysis, but questions arise in his mind as to what it really is and how it was made. The lack of answers leaves the matter quite ambiguous. He knows that duplicating the analysis will not insure duplicating quality. The analysis alone tells him but little of the details

red shortness, cold shortness and gas holes. These additions to simple steels always contain some carbon and manganese, usually some silicon, and may include aluminum, titanium or vanadium, one or more. Each of these elements, if added, is put in for some definite benefit to the metal. Collectively they are to suppress or at least diminish the harmful effects of oxides, silicates, sulfides, gases and segregation in the finished steel as well as to give the physical and mechanical properties desired. Their individual effects are set forth in Table 2. No two elements have identical roles.

TABLE 2.—*Statement as to Whether or Not Each Element Added to Simple Basic Steel is for Favorable Effect on Each Feature Noted*

Elements	Oxides	Silicates	Sulfides	Gases	Segre-gation	Mechanical Properties
Carbon.....	No	No	No	No	No	Yes
Manganese.....	Yes	Yes	Yes	No	No	Moderately
Silicon.....	Yes	Yes	No	Yes	Yes	Moderately
Aluminum.....	Yes	No	No	Yes	Yes	No
Titanium.....	Yes	Yes	No	Yes	Yes	No
Vanadium.....	Yes	Yes	No	Yes	No	Moderately

The elements aluminum and titanium, which are not added for direct effect on the mechanical properties, do indirectly have good effect on them by their action on the harmful impurities.

The purposes of the added elements in acid steels are the same except that silicon and titanium are not added to such steel for the elimination of silicates. In acid steel the manganese supplies the basic oxide needed for that purpose.

Carbon added would have a beneficial effect on the oxides in the bath metal by reducing some of them, in part at least, were sufficient time allowed, as it does in certain variations; but as ordinarily added the time thereafter is too short for it to have a noticeable effect on them.

Of the added elements, those which, when combined with oxygen, evolve more heat than iron per unit of weight will be oxidized and so consumed, wholly or in part. Carbon, even though its calorific power of 8100 cal. per kg. when burned to CO₂ is the greatest of all, seems to be an exception to this rule when enough silicon (which has a power of 7595 cal. per kg.) is present to kill the metal, which usually requires 0.25 per cent. or more. The silicon then seizes all the oxygen entering the metal because, in such an environment, and at such a temperature, carbon is oxidized, if at all, only to carbonic oxide (CO) in which case it generates only 2430 cal. per kg.

All the other elements named in Table 2 have greater calorific power than iron and therefore, after being added, are oxidized as stated, so

that an excess of each beyond that desired in the finished steel must be added.

The oxides formed from the additions are precipitated and they then agglomerate or coalesce with each other more or less completely in the well-known manner, the larger ones floating to the surface and merging with the slag, while the smaller, which rise too slowly for this in the time allowed, may be retained in the metal as sonims or non-metallic inclusions. As is the rule in chemical precipitations, agitation or stirring of the bath is helpful to aid the precipitated non-metallic matter to collect into large enough particles to rise; followed by a quiet period to allow them to do so.

Any copper, nickel, arsenic, or other element present or added, whose calorific power when oxidized is less than that of iron, is protected by the latter from oxidation and will persist in the steel. Any sulfur added which contacted with and so combined with iron would also be retained but for another reason; namely, because its affinity for iron at the bath temperature is greater than it is for oxygen. It does, of course, combine with manganese to some extent, the sulfide formed being insoluble in the metal so that its particles either escape to the slag or remain in the metal as sonims.

SOLID FINISHED STEEL

Next we will consider the constitution of solid, finished, though raw steel. Table 3 gives the non-ferrous constituents which may exist in it, showing that a piece even of simple steel may be quite a complex affair. The table contemplates only such concentrations as actually occur. An unduly high percentage of any element may be harmful whatever its state, or at least may render the steel unsuitable for its intended use.

While perhaps any of the gases, solubles and insolubles, shown in Table 3 may exist in any ingot of simple steel, the proximate ingredient which contains each of the five elements of the usual analysis is not ascertained. Table 3 shows therefore yet more of the reasons why such an analysis may give unreliable information about quality. All insolubles in steel, whether gases or solids are harmful. As already stated, the effect of any gases which are in solution in the metal is unknown.

There are also differences in effect of some of the ingredients according to whether they are residues of those in the charge materials, or are added later, as at the end. These effects may be their action on either the gases, or liquids or solids of the molten metal. Thus residual manganese and silicon may have had effect on the non-ferrous solids and liquids in the metal, particularly on the oxides, by furnishing other oxides for fluxing them as already described. The same elements may have checked the boil and so retarded the escape of harmful gases.

The true value of the ultimate analysis must be admitted, of course, for it is used almost universally in assigning steels to uses for which they are suited. But in that case it is supplemented by other knowledge of the metal and particularly of previous results obtained by the method by which the steel was made. No way appears, however, for detecting any abnormal heat of the specified composition which may result from slips or changes in conditions, such as whether the furnace is new or old,

TABLE 3.—*Occurrences of Non-ferrous Elements in Simple Ingots Steel State or Condition and Effect*

Elements	Gases		Solubles		Insolubles	
	State	Effect	State	Effect	State	Effect
Carbon.....	CO ₂ , CO in gas holes	Harmful	Carbide CO and CO ₂ Alloy	Useful ?	Graphite	Harmful
Manganese.....				Useful	Oxide Sulfide Silicate	Harmful Harmful Harmful
Silicon.....			Alloy or Silicide	Useful	Silica Silicates	Harmful Harmful
Sulfur.....			Sulfide	Mostly harmful	Manganese Sulfide	Harmful
Phosphorus.....			Phosphide	Mostly harmful	Phosphate	Harmful
Arsenic.....			Arsenide	Neutral		
Oxygen.....	CO and CO ₂ in gas holes	Harmful	Ferrous Oxide FeO	Harmful	SiO ₂ MnO Fe ₂ O ₃ Silicates	Harmful Harmful Harmful Harmful
Hydrogen.....	Gas holes	Harmful	Solution	?		
Nitrogen.....	N, NH ₃ in gas holes	Harmful	Nitride	Harmful	Nitride?	Harmful
Aluminum.....			Alloy	Useful	Oxide Silicate	Harmful Harmful
Titanium.....			Alloy	Useful	Oxide Nitride?	Harmful Harmful

changes in the composition of the crude iron, proportion of crude iron in the charge, changes in the final additions or in fuel, weather or men. The practice at one plant cannot be duplicated *in toto* at some other. Every steel maker in starting to work at some new (to him) plant finds that he has something to learn.

So a formula for calculating properties developed and used at one works cannot safely be assumed to be applicable to steel made at another from different ores, iron and scrap, with other fluxes and additions and under other conditions. It is not so reliable a method as to be a substitute for an actual test.

We will next consider the functions of each of the five elements which comprise the ultimate analysis.

FUNCTION OF CARBON

The great function of carbon in steel is to increase its tensility and hardness, first in its natural state and, secondly, to still further greatly increase those properties in heat-treated steel. This relation of carbon and iron is wholly unique in Nature, no other two elements having anything like the same effect on each other. The usefulness of this effect or relationship to mankind can hardly be overrated.

In annealed hypoeutectic steel, carbon exists combined with iron to form the metatal cementite, as is well known. That is its usual state. In the ingot, cementite is likely to be concentrated or segregated in some measure in the interfacial matter between the grains, causing, with other segregated ingredients, the weakness, lack of ductility, and other shortcomings known as ingotism. The resulting structure is characteristic of the higher carbon steels, and the larger the ingot, the more pronounced it is likely to be, because of the slower rate of freezing which affords time for the metal to reject the ferrous compounds and non-metallic ingredients.

For this reason ingots of the order of 50 or 100 tons weight are cast in iron molds to expedite cooling rather than in sand molds which for certain reasons would otherwise be preferred. Proper heating and hot working tend to correct or cure ingotism in ingot steel. In steel castings, suitable annealing will do so by causing the reabsorption of carbon from the cementite by the purer metal of the grains.

In hypereutectic steel, carbon sometimes separates in part from the iron in the form of graphite, in which state it acts like so much foreign matter, highly injurious to the quality. This occurs only in high-carbon steels, perhaps only in those containing over 1 per cent. The higher the carbon, the greater the tendency to separate. Such formation of graphite is generally caused by improper heating; specifically, holding the steel too long a time at a temperature just above the hardening point or about 720° C.

Any carbon combined with oxygen as carbonic acid or carbonic oxide and dissolved in steel of course would be included with the carbonic acid formed by burning the carbon when that element is determined by combustion. The amount, however, is probably too small to be detected by weight. Some investigators of the gases of steel have found so little of these gases that they have concluded that they are insoluble in solid steel. The killing action of silicon and aluminum seems nevertheless to be based on solution of the gases which, if true, indicates that some of them must be in the metal though in what state is a matter for speculation. Evidence about these gases is needed.

Carbon in iron as carbide also has a far greater effect in lowering its fusion point than has any other element—about 90° C. for 1 per cent.

Carbon in steel is also the direct cause of the mushy stage through which steel passes in melting or freezing, as shown by the carbon diagram. With practically no carbon, as in ingot iron, the lines denoting the beginning and end of fusion come together at about 1530° C., at which pure iron melts. They again come together when the carbon content is about 4.3 per cent. and the temperature is 1136° C. Between these limits of temperature and carbon, the metal is a mixture of solid and molten constituents of a mushy or plastic consistency.

FUNCTION OF MANGANESE

Manganese alloys with iron in all proportions, and forms a part of every kind of steel; it has been knowingly used for such purposes for nearly a century. Yet its functions even now are not fully understood. It has some effect in finished steel, but its action or behavior in the metal before and during casting are what largely determine its effect on the product. In studying these effects of manganese one must consider it in the charge materials, as residual, as added, and in the finished steel; then its four known functions in the bath and ingot; then its variations in killed, partly killed and rimming steels; then in the acid and basic processes; then in its minor attributes and in individual steels. Thus by permutation we have a large number of cases of manganese in the different kinds of steel, and in their various stages of progress, at least to review, even though we shall find that many of them are alike. We can refer now only to a few typical or outstanding ones.

In the Charge

If the steel is to be killed, manganese in the original charge materials should average over 1 per cent. For rimming steel it need be but half as much.

General Effects in Molten Steel

Manganese is the great preventer of red shortness, because of its inhibition and elimination of oxides of iron in molten steel, which it accomplishes, first, by intercepting and combining with entering oxygen which might otherwise form them, and second, by reducing those already formed to metallic iron, an equivalent of manganese oxide (MnO) being thereby formed in either case. This oxide is insoluble and therefore harmful to the quality; it calls for elimination, which requires that it be combined with an acid, which, by fluxing it, will form a product that will collect into particles large enough to float out. In the acid process there is usually emulsified silicic acid in the bath metal, which serves this purpose. In the basic process silicon should be added, which will, by its oxidation, form the acid needed.

In molten steel manganese has some solvent power on the contained gases or some of them, though not great enough to be of much help in preventing the formation of gas holes and so killing the metal. Through this property, together with its superior affinity for oxygen, it has some quieting effect on the boil during decarburization, exercising therein a somewhat obscure function. It also lowers slightly the fusion point of the metal.

Manganese may also effect a partial elimination of sulfur from the molten metal by decomposing sulfide of iron, forming insoluble sulfide of manganese, a part of which may reach and mingle with the slag; with which, however, it is immiscible.

Residual Manganese

With the percentages mentioned of manganese in the charge, some will remain in the metal at the end of the heat, which shows that some has been present throughout the melt where it has served to limit the concentration of iron oxides in the metal. For the best results, this continued presence of manganese is essential whatever the kind of steel.

For killed steel there seems to be no reasonable upper limit to the amount of residual manganese that may be in the metal at the end without harm, if not with benefit to the quality. I say "there seems to be," because, as manganese has a quieting effect on the boil and a proper boil may aid in the elimination of harmful non-metallics and gases, it is at least conceivable that the quiet boil resulting from excessively high residual manganese, say over 0.5 per cent., may be prejudicial to the quality of the product because of these retained impurities. This is, however, conjectural. Every steel melter wants what he considers a nice boil, or sequence of boils, of the bath, but can give no reason for his desire except that he finds that with such boils his results are best.

For effervescing rimming steel less residual manganese is needed than for killed and therefore less in the charge materials. The best percentage is not yet definitely determined, but in the common grades of basic steel lies probably between 0.10 and 0.20 per cent. It should be distinctly less than for killed steel as a more lively boil is needed. To decide what is best we need among other things full knowledge of the gases of low-carbon and low-silicon unfinished steels; both what they are and how they behave. This knowledge is almost wholly lacking. Acid steel that rimmed in well has been made with but 0.01 per cent. residual manganese.

It seems probable that a proper boil eliminates some of the gas which forms skinholes in the rimming steel ingot. On the degree of concentration of this gas in the metal depends the depth in from the surface at which it begins to separate in bubbles, which form holes, and on that depth much depends.

With high residual manganese, say 0.25 per cent., carbon in the metal may be oxidized only slowly and with difficulty below 0.12 per cent. This seems to be due to the power of manganese to seize much of the oxygen entering the metal, even though its calorific power when oxidized to MnO (1653 cal. per kg.) is less than that of carbon when oxidized to CO (2430 cal. per kg.).

In basic steel residual manganese is likely to be reinforced by some reduced from oxide in the slag by carbon in the metal. Some of this oxide may have come from ore added to supply oxygen. As much as 0.2 or 0.3 per cent. of manganese may be so reduced. In acid steel this is much less likely to happen, and when it does it is in smaller amount, less than 0.10 per cent. and only in charges containing at least 0.5 per cent. carbon, which are held molten in the furnace for hours without addition of oxides.

Added Manganese

Manganese added at the end of a heat may not always clean the steel of oxides as completely as it should, either because the amount is inadequate, which is seldom the case, or the time elapsed after its addition is too short. Of the manganese added, some is oxidized by oxide of iron in the slag and is so wasted except for its equivalent of iron, which it reduces to the metallic state. Some is oxidized by oxides of iron contained in the metal in exercising its therapeutic function and that part is of the utmost utility and importance. The remainder, which comprises the bulk of it, is alloyed with the iron of the charge to give the concentration desired in the finished steel. This excess, which is necessary to insure that the destruction and elision of the oxides of iron in the metal be reasonably prompt and complete, together with the residual manganese and any contained in silicate and sulfide sonims in the sample, the chemist reports as manganese. The analysis tells the amount but not its story.

Added Manganese in Rimming Steel

To low-carbon effervescent steel to be rimmed manganese is added at the end solely as a physic, or specifically to prevent red shortness, and not for any effect on the mechanical properties. For most uses the proportion aimed at should be about 0.4 per cent. in the finished steel. More than that, say over 0.5 per cent., may, through its solvent power on the gases, or some of them, check their escape and so inhibit the churning action in the mold which is necessary for it to rim in properly. As a consequence, the steel may rise in the mold, which is always a sign that gas holes are forming. If it rises immediately after teeming these are harmful skinholes. In the pig and scrap method, when ore has not been used for decarburization, less manganese will serve, or from 0.25 to 0.30 per cent.

If the boil in the furnace at the end is unduly vigorous, a small increase of manganese added may be beneficial, while if the boil is too gentle, ore is needed.

Steel for making welded pipe must rim in acceptably, though as regards welding a considerable latitude in manganese, say from 0.35 to 0.45 per cent., is allowable.

Low-carbon steel cast too hot may rise in the mold and be worthless because of skinholes, even though the manganese be as desired.

Finished Manganese

In well made finished simple steel of any grade, manganese raises tensility about 150 lb. per sq. in. for each point contained. Increasing manganese, within limits, enables steel to endure without harm a higher temperature when heated in a furnace for hot working. This latter effect, however, may be indirect and due to better deoxidation by the higher manganese, and consequently more complete freedom from red shortness, rather than to the manganese itself.

In killed and partly killed finished steel which is not to be hardened and tempered, the manganese content, which is usually the greater part of 1 per cent., is more than has really been needed for good quality, the excess being added to make up in a way for insufficient time after the final additions were made.

For steel to be hardened and tempered as it is in many tools, manganese should be lower; the percentage depending on the bulk of the piece to be quenched and the carbon content. When the steel has over 0.9 per cent. of carbon and the piece is massive, say several inches thick, the manganese should not exceed 0.3 per cent. Such steel must be made with due regard to quality and treatment and ample time must be allowed for the manganese to do its work. With higher manganese the piece is in danger of cracking in the hardening quenching. This danger becomes less as the carbon and thickness (or either of them) are diminished.

Lower manganese than expected in the finished steel, if due to an overoxidized bath, may be a sign of a tendency toward red shortness, while if due to increased lapse of time after the final additions were made it may indicate well deoxidized steel. In the latter case it may be due to an intelligent and successful effort to compensate for an overoxidized bath by allowing additional time for the manganese to do its work, more, but perhaps not enough, being added usually in an effort to compensate for that oxidized in the metal and slag. So a steel abnormally low in manganese may be of ordinary, or inferior, or excellent quality. The percentage of manganese determined by the chemist does not tell which.

In the olden days much poor steel was made in the effort to give it, when finished, the specified content of manganese, and, at the same

time, to be economical of ferromanganese. So the time after the manganese was added was likely to be cut too short for its proper effect, and a red-short tendency resulted. It was not generally recognized that it was the manganese utilized as noted which cured red shortness rather than that remaining in the finished steel.

The practice of adding manganese in the ladle instead of in the furnace, as had been customary, was introduced at that time for purposes of economy. When manganese is so added it must be done intelligently, with due regard to its functions, or the quality of the product may be inferior.

Four Functions of Manganese

The four principal known functions of manganese in the acid process are then:

1. To cure its red-short tendency by decomposing oxides of iron in the metal.
2. To provide a basic oxide for fluxing emulsified silicic acid in the molten metal.
3. To eliminate some of the sulfur.
4. To give the specified composition in the finished steel.

The solvent effect of manganese on the gases, particularly those of rimming steel, seems to be that in the bath it checks the boil, while in the mold it retards both effervescence and the separation of skinhole gas.

In the basic process the basic oxide of manganese formed needs the presence and action of an acid to eliminate it.

FUNCTION OF SILICON

The actual state of silicon in steel is more uncertain than that of any of the other four elements, particularly when the amount is small or under 0.05 per cent. Table 3 shows that it may be there as alloy, or silicide, or oxide, or as a silicate, one or more, but the analysis does not tell which. Any present may be residual from that in the charge materials, that is, if the charge has not boiled, or may have been added at or near the end. As already noted, some may have been added which has done its work improving quality, and after so doing has left the metal, thereby escaping the chemist.

Silicon is added to simple steel as a curative, and in so serving it may play one or more of several parts which we will note in detail later. It has also been thought to increase the resistance to corrosion of plain steel as it does in crude iron when high—up to 10 per cent. or more. If it does so act in steel it is a matter of minor importance, since the superior abilities of copper and chromium to that end have become recognized.

The actions and so the effects of silicon are so different in acid and basic steels that each must properly be considered by itself.

Residual Silicon in Acid Steel

Silicon in acid steel may be residual, or added, one or both. Residual may be present in such steel in either of two forms, one of which occurs only with low carbon and the other only with high.

When there is more than 0.01 per cent. silicon in low-carbon acid steel to which no silicon has been added, and the bath in the furnace has boiled, as it practically always does when the carbon is low, that silicon will pretty surely be in the form of silica remaining from that formed by oxidation of silicon in the charge materials. Most of the silica so formed has, of course, left the metal and entered the slag, but some has persisted in the metal because it was infusible at the bath temperature and there was not enough oxide of manganese present to flux it. This happens when the original charge has too little manganese, say less than 0.3 per cent., and no metallic manganese has been added. All of that element may have been oxidized and eliminated before all the silicon has been, for in such a case there will be sufficient emulsified silica in the metal to flux any oxide of manganese therein. Then any silicon oxidized later remains for the most part in the metal until the final addition of manganese is made. A part of that is oxidized and the oxide fluxes a part of the remaining silica, but 100 per cent. cannot be so eliminated. That remaining is highly injurious to quality, tending to make the steel red short when hot worked, and lessening ductility.

In making acid high-carbon steel such as that for springs, with from 0.8 to 1.0 per cent. of carbon, by the pig-and-scrap method, there must be a relatively large proportion of pig in the charge to provide the carbon desired. In that method no excess of carbon is intentionally added, but the quantity of pig to give that desired may also contain so much silicon that when all is melted the metal will still hold 0.3 or 0.4 per cent., which is enough to make it lie dead in the furnace. If the carbon content is right and the silicon not objectionable, the charge may be cast with that amount of residual silicon.

Some makers of springs object, however, to so much silicon in their steel, as it does not suit their tempering methods, and sometimes the carbon is much too high for the specification. In either case the silicon in the metal must be nearly all oxidized by added ore. Carbon cannot be oxidized in the presence of much silicon. If it is but little too high, say less than 0.1 per cent., it may be diluted by the addition of low-carbon scrap steel or wrought iron and made right without ore additions. When residual silicon in such a heat is unduly high, carbon is likely to be high also, as the case usually results from exceptionally quick melting and consequently less waste of the charge materials by oxidation.

Most unusual, but yet possible, is the case of an acid steel with high residual silicon, say from 0.6 to 1.0 per cent. or even more, and the ingot

badly infested with gas holes. Such a heat is made only in the pneumatic converter, when the charge in blowing becomes excessively hot, due usually to too much silicon in the crude iron. At an unduly high temperature, apparently around 1650° C., the affinity of silicon for oxygen is much weakened, if not destroyed, while that of carbon for oxygen is increased. Consequently, in a heat which reaches the critical temperature, the carbon in the iron is all burned out while a considerable part of the silicon remains in the metal unoxidized when the flame drops, which it does when the carbon is all consumed. The major part of the silicon is indeed oxidized before the temperature reaches the critical point but the unburnt residue may be as stated. The copious volumes of carbonic oxide and other gases formed or otherwise present have saturated even that great amount of silicon with all it can hold, so that as the metal solidifies in the mold enough is set free to form a profusion of gas holes as described. This case never occurs in open-hearth steel.

Added Silicon in Acid Steel

Silicon is added to plain acid steel (1) to kill it more or less perfectly and (2) sometimes as a step toward deoxidation. For killing, the proportion is usually something between 0.2 and 0.6 per cent. With less than 0.2 the steel is likely to be but partly killed unless the silicon is reinforced by the addition of some other gas solvent such as aluminum or titanium. With low carbon rather more solidifier is needed than with higher carbon.

This solidifying effect is sometimes called deoxidizing, but incorrectly so, as acid steel killed with silicon alone may be far from being deoxidized; being too red short to be of any use. Partial deoxidation with silicon is the reaction between that element and the oxides of iron in the unfinished steel resulting in the formation of silicic acid and the liberation of metallic iron. It takes place quickly after the silicon is melted and incorporated with the metal. The silicic acid formed is an infusible, non-metallic impurity which if permitted to remain in the metal is, like residual silica, more harmful to the properties than the oxides of iron it has decomposed. To eliminate it a basic oxide, or, particularly, oxide of manganese is needed to combine with and flux it, so that its particles may coalesce and escape.

For killing steel no time is required after the silicon is melted and mixed with the metal, as its solvent power becomes immediately effective. Probably no chemical action is involved. For this reason a large part may properly be added in the ladle. Some of the silicon added for killing the steel will, however, be oxidized, even with the addition of plenty of manganese to do the deoxidizing, and form silicates which, being minutely comminuted, leave the metal but slowly. For this reason a part of the

silicon should be added in the furnace so that the silicates so formed may have ample time to escape as completely as the desired quality of the steel demands. The power which silicon has to prevent the formation of gas holes and so to kill steel is explained in two ways:

1. If the gas to be suppressed is a compound, particularly carbonic oxide, which is the most plentiful gas in ordinary molten steel, it may conceivably be decomposed by the silicon with the formation of silicic acid, which is insoluble in the metal, and carbon which is soluble therein and therefore absorbed. Neither of these products is gaseous at the temperatures of molten steel. The action of silicon in preventing the formation of carbonic oxide is of course equivalent to its decomposition.

2. According to the other explanation, the silicon keeps the gaseous compounds in solution and so prevents their separation on freezing and thus their formation of gas holes. This usually, if not always, seems to be the correct explanation. Any elementary gas, such as hydrogen, must of course be kept in solution by the silicon.

Sometimes a part of the silicon in acid steel has been reduced from silica in the bottom or slag by the action of carbon in the metal. This may be as much as 0.1 or 0.2 per cent., or nearly enough to kill the steel. It happens only when the carbon content is comparatively high, or over 0.5 per cent., and the bath is held for some hours in the furnace without the addition of oxide of iron in any form. The slag then becomes strongly acid and vitreous, containing from 55 to 60 per cent. of silica. The bath is almost dead. Bubbles are few and each one bursts with an audible snap through the tough slag. Silicon in steel so reduced is a guarantee that the metal has been well purified of its oxides. In the acid electric furnace, under similar favoring conditions a still more rapid and more prolific reduction of silicon is likely to take place.

In the old method of melting crucible steel, which is still practiced to some extent, this manner of reducing silicon from the siliceous environment was the only way in which the metal acquired that element and was killed. Up to 0.6 per cent. or even more was sometimes so reduced. The average was perhaps between 0.3 and 0.4 per cent., which was quite enough to kill the steel, the maximum mentioned above being more than was needed.

Assuming apparently that silicon found by the chemist meant always the one thing, some crucible-steel makers have hastened the process and shortened the time for making a melt by adding the desired percentage of silicon to the charge in the form of ferrosilicon. They either put it in the pot with the cold charge or add it after the charge is melted. Whether these accelerated methods are equally good or whether either is as good as the old way, those who practice them may or may not be able to demonstrate. The silicon is undoubtedly alloyed with the iron or combined as silicide in all three cases alike; but the time required for

killing in the old way, which is largely saved by the newer methods, and the boiling action which the metal has when first melted, if the silicon be low, may be needed for, and aid in, cleaning the metal of its non-metallics and also possibly of some of its deleterious gases. This time and boil may tend to impart superior quality to the steel.

Holding the molten charge for killing by the absorption of silicon from the slag and walls is more practicable with clay pots than with those made of graphite because, during that period, too much carbon would be absorbed from the latter. This would waste the crucible, unduly shortening its life; and, as the amount of carbon thus entering the steel would be variable, the product might be too irregular in its content of that element for commercial practice.

In well made, finished simple steel, silicon raises tensility about 150 lb. per sq. in. for each point contained. This effect is sometimes not attained in steels of poorer quality, being masked by more or less abundant non-ferrous or non-metallic impurities remaining in the steel. Silicon is not added primarily to give increased strength to plain steel, carbon being six or seven times as effective for that purpose, which indicates that silicon is alloyed with the iron and not combined as carbon is.

Residual Silicon in Basic Steel

In basic open-hearth steel neither of the cases of residual silicon which occur in acid steel as noted will be encountered. Any notable amount of silicon found in basic steel has been added to it at or near the end. As residual it is rarely if ever present; certainly never in any steel from which an excess of carbon has been eliminated by oxidation, as is almost universally the case; for, as we have noted in the case of acid steel, practically all the silicon must be oxidized before much carbon can be.

There is not enough acid to flux all the basic oxides of iron and manganese which impregnate the metal at the end. The basic environment, both hearth and slag, absorbs substantially all the silica from the metal early in the course of the heat. An acid is therefore called for, as we have noted.

The chemist may indeed report 0.005 per cent. in the finished steel, an exceedingly small amount, which, if really present, may be in the form of emulsified silica or silicate. He cannot tell if the silicon he finds is combined with iron or oxygen.

Added Silicon in Basic Steel

Silicon may or should be added to basic steel shortly before the end for several different purposes, as follows:

1. To prevent further oxidation of carbon. This addition is made in the furnace and is to hold the charge as it is chemically, excepting the oxidation of the silicon itself, while the bath metal is being analyzed. Oxygen which reaches the metal after the added silicon is incorporated with it is seized by that element, none being available for oxidation of carbon.

2. To help deoxidize the unfinished steel. For this purpose, which is to minimize red shortness, any quantity up to 0.15 per cent. may be added in the furnace. While manganese is the great deoxidizer, silicon is generally held to aid. Alone, however, unless considerable residual manganese is present, it is not efficacious.

3. To form an acid which will flux and so promote the elimination of basic oxides from the molten metal. This important function must be considered together with that of deoxidizing which it follows. The oxides of manganese and iron present are both basic and have no affinity for each other. They need an acid to flux them and so enable them to coalesce and escape. Any silicon added up to 0.15 per cent. to stop the boil of a basic bath is largely oxidized during the time the charge is held, even though the boil may not have recommenced; 0.02 per cent. of silicon so remaining is enough to keep the bath quiet even though 0.12 or 0.15 per cent. was required to practically stop the boil. The silicic acid formed serves to elide the basic oxides as noted. Ordinary ferromanganese or spiegel usually contains some silicon which is oxidized before the manganese and serves the same way after addition. It is usually better, however, to insure an ample supply by adding additional silicon; which, however, in freeing the metal of oxide may have left it, so that it will not be found by the chemist.

In acid steel, if additional silicon is required, the need is not so pressing or universal as in the case of basic.

4. To prevent the formation of gas holes. To avoid undue loss, and so to do this effectively, the silicon for this must be added in the ladle. It acts much as it does in acid steel but more is oxidized in the metal and slag. The oxide of iron in the latter tends to oxidize carbon as well, making more gas for the silicon to hold in solution; so a somewhat larger percentage of it is needed to kill basic steel than acid steel, or about a fifth more.

The first function is a manufacturing convenience. The other three are all curative. In a moderate degree, silicon also lowers the fusion temperature and gives heat to the metal by its oxidation.

Time Required for Different Functions of Silicon

After an addition of silicon is melted and mixed with the molten metal, the time required for it to exercise its various functions varies greatly:

1. To retain gases in solution and to check further oxidation of carbon the action is immediate—practically instantaneous.
2. To decompose oxide of iron in solution is a matter of seconds.
3. To form silicates of iron and manganese is a matter of minutes. This includes the fluxing and merging of emulsified oxides by the fluid silicates first formed.
4. To clean the metal of silicates completely is a matter of hours.

Some effects of high temperature on the affinities of silicon, carbon and oxygen for each other in iron metallurgy are indicated in Table 4. The reaction is reversible according to the formula

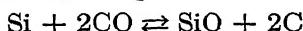


TABLE 4.—*Chemical Relations of Silicon, Carbon and Oxygen as Affected by High Temperatures*

TEMPERATURE, DEGREES CENTIGRADE	BEHAVIOR
700	Silicon reduces CO in the laboratory, forming SiO_2 and liberating carbon.
1550	Silicon prevents the formation of CO in the open-hearth bath and so tends to kill the metal.
1600	Carbon reduces silicon moderately from slag and hearth in the acid, open-hearth crucible and electric processes.
1650	Carbon prevents oxidation of silicon in the bessemer blow. Perhaps reduces it.
1900	Carbon reduces silicon freely from its oxide in the blast furnace.

Below the equilibrium temperature of the reaction of silicon with carbonic oxide, which seems to be in the neighborhood of 1600° C., the affinity of silicon for oxygen is stronger than that of carbon, while above it the affinity of carbon excels.

It appears, therefore, that the percentage of silicon reported by the chemist requires supplementary information to give its full meaning. To appreciate its significance one must know how it came to be in the steel.

FUNCTIONS OF SULFUR AND PHOSPHORUS

The percentages of sulfur and phosphorus usually stand for what they are. The only points in doubt are whether they are residual or added. If the latter, they are thought to work less damage to the ductility of the steel than if residual.

Added phosphorus is held to have some deoxidizing effect on the steel and, if there is a deficiency of silica, its oxide may serve as an acid to flux basic oxides in the metal, as does silica. This action may be the basis of the commonly held opinion that added phosphorus does not make the steel as cold short as residual; but as ferrophosphorus always contains some silicon, it may be that phosphorus gets credit that rightfully belongs to silicon.

When more than 0.05 per cent. of either of these elements is present in basic steel, some has probably been added to promote machinability, or, in the case of phosphorus in thin sheets, to keep them from sticking together too strongly when rolled doubled. An excess of each is needed in either case because a part of the phosphorus so added to basic steel is oxidized, while a part of any added sulfur is volatilized.

SUBJECTS FOR RESEARCH

During this talk we have considered some things the ultimate analysis does not tell us regarding the make-up of steel, including:

1. The genesis, composition, behavior and effects of the various gases, both in gas holes and in solution.
2. The genesis, composition, manner of occurrence and effects of the various sonims.

These are subjects worthy of research. But let us urge that in studying them the history of the steels dealt with, particularly the furnace practice by which they were made, in all details, be noted and recorded as fully and as clearly as can be done by language, to the end that the man in the shop may be enabled to utilize the results in his work —to apply the good and avoid the bad.

Improvements in Blast Furnace Construction

BY J. P. DOVEL,* BIRMINGHAM, ALA.

(New York Meeting, February, 1928)

HAVING been requested to prepare a paper referring especially to my patents as applied to blast furnaces, I shall confine my discussion to those improvements and inventions pertaining directly to the blast furnace itself, omitting a number of patents pertaining to blast furnace operations. I spent the early part of my life in the construction of blast furnaces, from rivet-heating to drafting and designing, much of the work relating to repairs and rebuilding. Later, as I became more interested in maintenance and operation of a group of blast furnaces, one fact especially made a lasting impression on me; namely, that a very expensive piece of equipment was very short lived, and the expense of replacement, relining, etc., in many instances consumed most of the profits made while in actual operation. As far back as 1910, I began to lay plans to build with a view to permanency and not merely for a blast, the common expression at that time, which really meant only one or two years in southern practice. Since we did not then blow so hard most failures occurred in the bosh and hearth. The failure of either generally meant a complete new lining, as the inwall did not look good enough to last another blast.

At that time we were using two types of hearth, one of heavy steel plate protected by well and sprays on the outside, and one of heavy cast iron, made in sections and bound together with wrought-iron bands. The former type proved dangerous, for if the iron should come through, as it frequently did, it would cut away the steel plate, quickly turning large quantities of molten iron into the water, causing a severe explosion and costly repairs. The cast-iron type gave trouble also by the iron finding its way through the joints between the sections, which was not so serious; since the iron would not cut away the heavy cast-iron sections very quickly, and generally caused only small damage, and repairs were easily made. Both types have been improved; the former by the introduction of cast-iron water-cooled plates, placed on the inside of the steel jacket. This has proved to be very good construction, but has no real claim to permanency. As the cast-iron plates cannot be replaced from the outside, the operator must assume that some time, at no late date, he must replace them from the inside, which will mean a blowing out of the furnace. The heavy cast-iron hearth has been improved by making the

* Vice-president, Sloss-Sheffield Steel & Iron Co.

sections very thick. With machined and lap joints, and bound together securely, nothing can happen that cannot be repaired from the outside without blowing out. This means a permanent hearth and some are now 17 years old.

Bosh construction has been improved until the whole bosh is encased in metal and does not depend upon its brickwork to any great extent. The oldest of this construction is 11 years old, still in service in perfect condition, and many more years will be required to determine just how permanent it is.

The improvements referred to above do not represent inventions on my part, except with minor exceptions, but were mostly selected from what we had at the time and simply built better and with a view to permanency. However, the fact that they are so arranged that the structure is permanent and that they maintain a stationary working line in connection with the permanent lines above the bosh makes them an essential feature of my improved blast furnace and process.

At the time that operators began to blow blast furnaces harder, causing frequent and early failures in inwall sections just above the mantel, the real problems in producing a permanent blast furnace appeared almost insurmountable, as failures were frequent and apparently there were no means to prevent them or to repair without a costly blowout and relining. Several moves were promptly made to obviate this disastrous result, one of which was to embed cast-iron water-cooled blocks in the wall. This appeared good, but for a short while only, as in many cases the brick would fail just the same, resulting in the failure of the blocks also, and producing an even more serious condition than if the blocks had not been used. This method was promptly abandoned by some of our well-known engineers. Another method came into almost general use and might be said to be in almost general use at the present time. This consisted in using thicker inwalls and larger bells so as to place the ore next to the wall, causing the furnace to work through the center. As this method protected the brick from the heat and blast, it prolonged the life of the furnace but not to a degree of permanency. I think that I can safely say that it increased the amount of flue dust and also of off-grade iron.

None of this work helped me in producing a permanent blast furnace. What was really helpful was a series of early inwall failures on a group of furnaces that I was operating. Something had to be done. I was brought face to face with the fact that no brick are good enough to meet the requirements of present-day blast furnace operations, and the better the operation the more quickly the inwall may fail. I could not continue to reline these furnaces, and my dream of a permanent blast furnace was glimmering, when the idea of rebuilding the lining while in operation occurred. This was done by the insertion of a series of rows of bronze cooling-plates from the outside, attached to and supported by the shell.

This promptly agglomerated the material about the plates and rebuilt the linings to the desired dimensions and, as I believe, permanently. The first were put in service in 1922 in a furnace that had inwall failure at the time. They are permanent over this period and in good condition.

With a permanent hearth, a permanent bosh, and a permanent inwall only the top section remained to complete my permanent blast furnace. This was accomplished by discarding the brick in the top section and substituting a heavy cast-steel jacket lined with cast-iron blocks, which does withstand the wear and maintains a permanent stock-line. Thus having established a permanent and indestructible stock-line, stock distribution without regard to the brickwork has been made possible, resulting in greatly increased areas in existing stacks in the upper section, which has proved so desirable. Nearly all blast furnaces as at present constructed can be converted to this type, resulting in increased areas in the upper section of the furnace, together with a rearrangement of stock-lines with sufficient area to permit the free passage of the gas through the natural voids in the column of stock without disturbance to it, also with stock distribution as to cause the gases to flow approximately uniformly through the entire column of stock in such way as to produce a temperature around the column of stock of approximately the same as or a little greater than that within the column, producing practically a uniform rate of reduction throughout the entire mass. With volume of charge so proportioned as to maintain this uniform rate of gas flow and uniform temperature, this has resulted in reducing the amount of flue dust produced by 90 per cent., has reduced coke consumption as much as 16 per cent., and has increased production by 30 per cent. It has also made possible the use of a larger percentage of very fine ore and creates an ideal operating condition; as slipping, with consequent burning of bronze and the production of off-grade iron, has been practically eliminated.

Having thus described my improved furnace as briefly as possible, the comment may be added that these improvements have come at a very opportune time, as competition, both domestic and foreign, is becoming keener. Happily there is no desire on the part of operators to reduce wages or lower the standard of living in this country, which would react to lower the consumption of iron. On account of the cost of assembling raw materials and readjustment of industrial conditions some plants are becoming obsolete, and the tonnage they produce will have to be made up by additional furnaces or increased capacity of existing furnaces. This situation can be met without additional new furnaces through the gradual changing of the present type good furnaces into the improved type at a moderate expense. In many cases this will add nothing to capital account, since the amount ordinarily set up for relining will cover the entire expense over a very short period of time, as has been proved by actual performance on several furnaces changed to this type.

DISCUSSION

C. A. MEISSNER, New York, N. Y.—We have had occasion recently to study more closely some of the southern construction. Of course, we must not forget that the conditions of operation in the South are very different from the conditions that we have in the North. Ores are different. Few furnaces in the North have hard ores. As to the hearth and bosh construction, just how that will apply to our large furnaces we are not quite sure, though I think Mr. Dovel has made a great deal of improvement in that direction, especially for his conditions.

What interested us particularly was the enlargement of the upper area of the furnace. Flue-dust production is one of the very serious bugbears for our northern furnace. It is very heavy and represents a high ore cost. Our flue dust runs 45 or 50 per cent. in iron. In the South, it runs 30 or 35 per cent. That means to us a heavy loss of ore that we have paid for. We do not expect to have anything like 90 per cent. reduction in flue dust, such as Mr. Dovel obtained (and I think from the figures we saw that he is perfectly correct in his own practice) but even 40 per cent. reduction would help us.

Mr. Dovel enlarged his stock-line. For example, where we have ordinarily a 17-ft. stock-line, he has 18 and $1\frac{1}{2}$ ft. Then he decreased the size of his bell. In other words, he gives himself a lot of room between the bell and the stock-line and also a lot of room at the top. For instance, where he has a speed of gas, say of 6 ft. per sec., we have a speed of gas running to 10, 11 and 12 ft. per sec. His stock-line protection has been very satisfactory in the South and a number of our furnaces are using it. He has certainly blazed the way more definitely than has been done heretofore in the possibilities of the enlargement of stock-lines.

Whether the decreasing of bells is advisable or not, we do not know. We are going to try it. We will have some smaller bells put in, for it is a simple matter to change the bell and put in a larger one if necessary.

Mr. Dovel has been working on a good many other things, too; one being an impinging gas cleaner with which he gets good results. Whether it will work as well with our condition of flue dust, we do not know, but I think it is well worth studying.

G. P. HANSEN, Ashland, Ky.—It may be of interest to the persons attending this session to know the conditions that existed at the Portsmouth furnace of the Wheeling Steel Corp. The inwall was very badly burnt out and it had come to a point where they seriously considered blowing out the furnace for repair. Mr. Dovel's inwall plates were inserted and the furnace has been operating satisfactorily for a year and a half without indications of hot spots.

I spent some time with Mr. Dovel in Birmingham. His rearrangement of his furnace is extremely interesting. When one considers that the top 20 or 25 ft. of the furnace is not firebrick, but consists of a jacket with cooling plates inserted, one can readily see what he is getting to on a stock-line.

The general subject, as Mr. Meissner pointed out, will certainly bear study and we will watch it with a great deal of interest.

R. FRANCHOT.—Did I understand you to say that the top of the furnace is not lined with brick?

G. P. HANSEN.—Yes; 20 ft. unlined.

R. FRANCHOT.—That point is very interesting. In studying solution loss, sometimes sight is lost of the fact that what is calculated as a solution loss is a net effect between carbon gasified by CO_2 and carbon deposited by the decomposition of CO . Theoretically, it would probably pay to promote, as far as possible, the decomposition of CO if it can be done without too much plugging up of the ore, because although

This reaction is an exothermic one and develops heat, which in the absence of an increase of burden would be lost, still the carbon deposited increases the proportion of coke reaching the tuyeres burning with air to give hearth heat, and on the whole the action would probably be beneficial. In that connection the lack of insulation in the top of the furnace, if it has been tried out and found to be not harmful, is very interesting.

G. P. HANSEN.—I cannot be sure of the exact figures, but Mr. Dovel told me that in blowing out one of the city furnaces he had reached a temperature of some 900° to 1000° on top, with no harmful effects on his steel castings. Incidentally—I cannot be sure of this figure either—but I think he told me flue dust recovered had been reduced from some 400 lb. per ton to approximately 91 lb. per ton, but he charged that to the wider top.

J. P. DOVEL (written discussion).—Recent experimental work with our blast furnace consists principally of recrushing the hard ore that we use as a basis of our furnace burden from 2 or 3 in. and under to that of $\frac{3}{4}$ in. and under. We are also carrying on experiments in grinding the ore to pass 20 mesh. At the present time we seem to have established the fact conclusively as applied to our conditions that the finer the ore the less fuel is required in reducing. This statement is undoubtedly correct from a thermal efficiency standpoint. The work we are doing now is intended to match this principle with the practical conditions; in other words, we are trying to determine just how fine this ore should be crushed. We reduced coke consumption approximately 300 lb. per ton of iron by crushing the ore down to pass $\frac{3}{4}$ in. mesh. We got almost similar results by charging 25 per cent. of ore ground to pass 20 mesh with the coarse ore (from 2 to 3 in. and under). We expected that this peculiar and rather radical preparation of stock would produce a very bad dust condition. In this we were very agreeably surprised, as little difference in the amount of dust thrown was indicated. We are doing a good deal of experimental work along this line and will be very much pleased to describe what we have done and what the results have been just as soon as we get this information in concrete form.

Referring to the fourth paragraph in Mr. Meissner's letter, I am of the opinion that very few furnaces would show much improvement merely by the use of smaller bells; however, it might benefit in some cases. The theory of this method is based on the fact that the stock column should present a larger void area through the stock where the gas must pass, sufficient to slow down the flow of the gases through the column of stock to such an extent that the gases will not entrain the dust as they pass through. Of course it would be extremely desirable that these void areas in the column of stock should be uniform throughout. This condition would be almost impossible to obtain. The nearest that we can approach is to charge the ore burden in such way that it will just roll to the wall on the outside and just to the center on the inside. This insures a free passage of gas around the column and through its center. With this condition we have obtained the best results that have ever come under my observation, by reaching the extreme low point of flue-dust production over a period of 30 days of 24.6 lb. per ton of iron. Strange as it may seem, this was only slightly increased by the addition of 20 per cent. of the charge of ore ground in a rod mill to pass 20 mesh.

The great reduction in fuel consumption accomplished with this furnace is about 50 per cent., due to cutting down production of flue dust, which ranged from 400 to 550 lb. of iron, about half of which was coke; the other portion of the fuel reduction I attribute to the fact that we heat the column of stock almost uniformly around the outside as well as through the middle.

The reason this furnace does not slip or blow through is also due to the fact that we carry on a rate of reduction around the column of about the same speed as the

rate of reduction through the column. This fact is equally responsible for the reduction in flue dust, as a furnace operating steadily would not, under any condition, produce as much flue dust as one that operated or moved intermittently and violently.

Mr. Meissner also refers to the gas cleaner that we are using. The experimental work that we are doing in crushing the ore, and readily producing fine-mesh ore, will also have an effect on the gas cleaner. We anticipate that whatever this effect may be it will be almost insignificant, as this gas cleaner produced good results and kept the stoves clean when we were making ten times as much flue dust as we will make even with fine ore. This gas cleaning is a dry cleaning process and over a period of ten years has kept the stoves clean and in good condition. However, we will present some exact data in reference to results obtained with this method.

Mr. Hansen refers to results obtained by my inwall cooling system on the Portsmouth furnace. This is just in keeping with what is taking place on 23 other furnaces, all of which have been successful. It might be well to state here that the inwall cooling system is an absolute necessity in connection with a furnace where the distribution is such that reduction takes place around the column as well as through the center, as there is no brick that will stand this condition; therefore the inwall must be thoroughly protected in some way or the furnace would soon be a failure in its inwall. The indestructible inwall has made possible the large-top blast furnace. Probably the condition that is responsible for the metal top arrangement in this furnace is due to the fact that few blast furnaces in their present condition can be changed to this style without building a new shell, while most blast furnaces can be converted to this type of furnace with the present shell by the use of the metal top construction. Of course, a large top could be produced by the old method but the brickwork would not stay put without some type of top protection. I deem it very essential that this top line should remain absolutely where it is intended to be, as correct distribution cannot be obtained with an irregular top stock-line.

Cleaning Blast-furnace Gas

BY ARTHUR J. BOYNTON,* CHICAGO, ILL.

(New York Meeting, February, 1928)

IN THE preparation of this paper the writer has been influenced by the fact that descriptions of various means of cleaning blast-furnace gas have been published and that further descriptive treatment of the subject will probably be less interesting than a statement of conclusions with regard to preferable methods which have been reached by him as a result of experience and observation in this country and also as a result of somewhat detailed investigation of the subject made toward the end of the year 1927 on the Continent of Europe and particularly in Germany. Owing to various circumstances, including a cost of fuel that is extremely high in relation to the wages of labor, the German iron and steel industry has accumulated experience in gas washing which is as yet in part lacking in the United States of America. The paper begins with a statement regarding the economics of the use of blast-furnace gas, then considers the principles and practices employed in its purification.

USES OF BLAST-FURNACE GAS

For many reasons having to do with the utilization of coke-oven and blast-furnace gases in steel manufacture and with the use of hot metal, the blast furnace is now usually a part of a steel-producing unit, which also includes coke plant and rolling mill. Therefore both blast-furnace and coke-oven gas are usually applicable to any of the iron and steel-making processes, including the generation of power, and their allocation in any given works should be considered as a single problem. The uses to which blast-furnace gas, either alone or mixed with coke-oven gas may be put, include the following:

Regenerative Heating of Air for the Blast Furnace.—This is the oldest and metallurgically the most important of all uses. It is universally performed with unmixed blast-furnace gas and under proper conditions should require not over 23.5 per cent. of the total gas generated for a blast temperature of 1350° F.

For Steam-raising Purposes.—This is almost universally done with unmixed blast-furnace gas. From the standpoint of quantity used, it is at the present time the most important application in American steel-works practice.

* Vice-president, H. A. Brassert & Co.

In Gas Engines for Blowing and Power.—While there have been large-scale installations of gas engines in the United States, the use and renewal of which still continue, the tendency in recent years has been to take advantage of the marked improvement in boiler construction and operation and of increased size and efficiency in the steam turbine and to install steam-driven units for both blowing and power. Even although the present tendency is toward the use of steam, the large number of gas engines installed and the advantage of washing to a high degree of cleanliness at minimum cost, makes improved methods of gas cleaning of great interest in connection with this use.

Underfiring of Coke Ovens.—This may be carried on with either straight blast-furnace gas or with a mixture of coke-oven and blast-furnace gases. The use of straight blast-furnace gas for this purpose is now more than 12 years old in Germany and its application in this country has been definitely proposed, although no American plant is as yet operating under these conditions. The advantages of straight blast-furnace gas include a greater ease of regulation of the oven operation and a generally more uniform heating, with consequent benefit to the character of the coke. This is due to the large percentage of inert in the products of combustion of blast-furnace gas and the consequently increased length of the flame.

In the Manufacture of Open-hearth Steel.—Proper use of blast-furnace gas mixed with coke-oven gas in the manufacture of open-hearth steel requires a variation in the percentage of coke-oven gas contained in the fuel mixture in accordance with the stage of the open-hearth process. No single fuel has obtained the heat economy in the open hearth that is possible with mixtures of blast-furnace and coke-oven gas under these circumstances.

For Mill Heating.—The range of heating operations to which blast-furnace and coke-oven gases have been successfully applied includes all processes from the soaking pit to sheet and pair furnaces in the sheet mill. In mill heating the proportions of the mixture are held constant for any given operation, but are varied in accordance with the temperature of the steel entering the furnace, the temperature to which it is desired to heat, the necessary speed of heating and the size of the steel.

Comparison of Uses

Of these uses, application to hot-blast stoves and to boilers may be made without other cleaning than that obtainable through wet scrubbers, but at the sacrifice of ultimate refinement and efficiency of operation. For open-hearth and mill use, as well as for stoves of refined design, a secondary fine washing has been found necessary wherever such applications of blast-furnace gas have been made. In the case of gas engines and coke-oven underfiring, a very high degree of cleaning is necessary.

The choice of uses to which blast-furnace gas should be put for the realization of the greatest possible benefit depends in great degree on local circumstances. In every case, however, decision should be made in accordance with certain broad principles. In all cases the primary use of blast-furnace gas will be for regeneration of the hot blast. No economical substitute for blast-furnace gas for this use has been proposed.

With regard to steam generation, it is necessary to consider that blast-furnace gas with a very slight admixture of coke-oven gas is a perfect substitute for producer gas, while at the same time its employment avoids the expense of producer installation and operation, and a loss in the producer which runs from 10 to 25 per cent. of the fuel charged in accordance as the producer gas is used hot or is cooled prior to use. On the other hand, the preparation and use of solid fuel under boilers either in stokers or as powdered coal involves less expense for installation and operation than is involved in the producer operation for the same quantity of coal. It is also to be noted that solid fuel is more economical and capable of giving a higher boiler efficiency, as well as a greater production from the same boiler, than is blast-furnace gas. The tendency toward higher pressures and more superheat in steam will increase these differences, excepting as preheat is applied both to air and gas, the latter condition being possible of fulfillment only with finely washed gas. In general, therefore, it appears that blast-furnace gas is best used in a process where gaseous fuel is recognized as necessary rather than as a substitute for solid fuel in a process in which the latter is capable of giving better results.

The other uses include the driving of gas engines, underfiring of coke ovens, and open-hearth and mill heating. In so far as gas engines are installed or may be installed, for reasons of which a discussion is beyond the scope of this paper, blast-furnace gas will be allocated to this use. Such gas will be washed to the highest degree of cleanliness possible.

The advisability of using blast-furnace gas for underfiring coke ovens will depend on the relative value of the two gases for other purposes. Where by-product gas can be sold to a public service company at a price that is based not only on its heat value but also on economy of transportation and convenience in use, it will be advantageous to underfire the ovens with blast-furnace gas. This use also makes possible the conservation of gas at week-ends or during periods of slack demands with a holder capacity one-sixth the size of that necessary for an equal heat value contained in blast-furnace gas.

Where no outside sale of coke-oven gas is contemplated and where both blast-furnace and coke-oven gas require use within the manufacturing plant, blast-furnace gas is best allocated to the steel works and the heating furnaces for use in mixture with coke-oven gas. This procedure enables a special fuel best adapted to each operation to be obtained by

proper proportioning of the mixture, and the thermal results obtainable are superior to those which can possibly be obtained by the use of either gas singly or by the use of producer gas. The logical order of use of blast-furnace gas is accordingly as follows:

1. Hot-blast stoves.
2. Gas engines, where such engines exist.
3. Open-hearth and mill heating.
4. Coke-oven underfiring.
5. Use under boilers.

As mentioned before, a certain latitude with regard to conclusion as to the relative desirability of use for steelworks and mill heating and for coke ovens is necessary in accordance with the circumstances existing at any particular plant. With this exception, however, the order of uses is logical under the circumstances usually existing.

CONDITIONS OF GAS WASHING

Determination of the most advantageous means possible to employ in washing blast-furnace gas requires consideration of several fundamental conditions, including the necessity of eliminating silica, alumina, lime and other slag-forming materials as well as metals, particularly manganese, which exist in the hot gases as vapors, and which are condensed into finely divided fumes upon cooling. These vapors begin to condense at the temperatures existing in the mains of the gas system prior to cooling and give rise to the condition practically known as "smoky gas," which is well known to be extremely difficult to burn. The complete condensation of these vapors requires the cooling of the gas to a temperature of approximately 200° F., and gas washing in the true sense can therefore not be accomplished at higher temperatures.

The necessity of cooling to 200° presents a problem with regard to the advisability of further cooling in order to obtain maximum useful heat effect from a given volume of dry gas and also maximum temperature of combustion. This problem arises as a result of the inevitable inclusion of water vapor in the gases as they come from the blast furnace. This water vapor, excepting as hydrogen may be formed in the upper part of the furnace, corresponds to the total content of moisture in the blast-furnace charge and of combined water in the ore and possibly in the limestone, plus the water which in American practice is added to the charge for the purpose of controlling the top temperature. This water vapor will constitute at least 10 per cent. by volume of the top gases and in the case of many American furnaces where water is added to the stock without exact measurement it may very considerably exceed this figure.

In considering the means proper to employ in handling this water vapor, it is advisable to point out a fallacy which has often been stated

in connection with so-called methods of dry washing. Advocates of these systems have claimed an advantage for such methods on account of the retention in the gas of sensible heat. Even although it were possible to wash gas completely at the temperatures at which it issues from the blast-furnace top, *the presence of water vapor involves a heat loss greater than any possible gain through high temperature of the gas as used.* This is true for all temperatures that correspond to reasonably good blast-furnace practice. It is still more true in view of the fact, as stated above, that cooling to 200° F. is necessary in order to eliminate slag vapors from the gas. Cooling to such a temperature involves a loss of much of the sensible heat originally contained, while the temperature in question is still above the dew point of the gas. It follows that the advantage of sensible heat is necessarily lost in part, while the disadvantage of water-vapor content remains in full measure.

The disadvantages in use of the content of water vapor in gas cleaned above the dew point include the necessity of heating the water vapor to the temperature of combustion, using heat which can be only partly recovered, in view of the higher temperatures at which the products of combustion issue from industrial furnaces. They also include the lowering of the maximum flame temperature possible to obtain with gas of a given composition exclusive of water vapor.

A third disadvantage results from the fact that the temperature of combustion of the blast-furnace gases lies within the range of temperature at which water vapor is dissociated and hydrogen formed. This decomposition of water involves a very serious heat loss which cannot be practically neutralized by subsequent combustion of the hydrogen at a lower temperature and at a later period in the heating process. Such combustion is likely to take place in the chimney flue or in the chimney itself and thereby to cause an undesirable temperature at these points.

Failure to eliminate water vapor from the gas in the washing process may also result in its condensation in the process of transmission from the washing plant to the point of combustion, with the result that liquid water is projected into the stove, boiler or other industrial furnace, and both the pyrometric effect and the recovery of heat further impaired.

It follows therefore that all processes of gas washing, whether dry or wet, which contemplate practically complete cleaning must include means for cooling the gas to the lowest practicable temperature, which will usually be below 90° F. At this temperature the maximum possible content of water vapor is 4.5 per cent., as compared with 10 per cent. or more in gas above the dew point. The reduction in temperature and in moisture content will result in the practical attainment both of higher temperatures and of a more efficient recovery of the heat contained in a given volume of gas under circumstances otherwise the same.

Comparison of various methods and processes of gas washing including the so-called wet, dry and electrical precipitation methods should be predicated therefore upon an equal degree of cooling of the gas prior to use.

It follows that both the dry filter or bag and the electrical precipitation processes are forced to use the same amount of water for cooling purposes employed by the so-called wet method, in order to produce washed gas of equal value.

Another underlying condition of all systems of gas washing is the economical recovery and disposition of the dust separated from the gases. The coarser particles of dust have a high metallurgical value on account of their content of iron and also of coke breeze, the latter permitting sintering without additional expense for fuel. The finer particles of flue dust are less rich in iron and are extremely difficult to sinter by present methods, this difficulty involving a smaller amount of product from a given sintering plant and a deterioration in the quality of the sinter produced which, generally speaking, makes treatment by this process uneconomical. It is important, therefore, if possible, to separate grades of dust that are capable of reuse as ore through sintering from those which are merely refuse.

The elimination of the coarser dust from the gas by processes of dry separation is also important, as it tends to reduce the expense incident to recovery as wet sludge. The cooling of the gas after purification, as practiced in the dry and electrical systems, fulfills this condition better than does the wet cleaning system as heretofore practiced. The development of means for effecting further separation of dust by dry methods prior to preliminary scrubbing is probably the most important improvement that can be made in wet washing methods.

The necessary and desirable conditions of gas cleaning may be summarized as follows:

1. Cooling to 200° F. for the condensation of slag and metal vapors.
2. Further cooling to lowest practicable temperature for the elimination of water vapor.
3. Classification of dust in order to permit an economical recovery of contained values.
4. The reduction of the amount of dust necessary to handle as wet sludge.

GAS WASHING IN EUROPE

Much of the practical experience which has indicated the relative advantages of the various possible uses of blast-furnace gas has been obtained on the Continent, and particularly in Germany, where the modern gas engine, as well as the science and art of gas washing as at present practiced, had its origin. Here economic conditions, including

a high cost of fuel, forbade the use of blast-furnace gas on any basis but that which afforded maximum recovery of heat value. The recognition of this necessity, and the successful study of the manifold conditions involved in the solution of its problems, are in accordance with the scientific spirit which has always actuated the German iron and steel industry.

The gas engine was the first important development in the direction of heat economy. Under the conditions existing, its use was immensely profitable, and its general adoption in German and Belgian iron and steel plants followed, although the use of the steam boiler still continued for the production of steam for coke ovens, for use in mills not yet electrified and for turbine-driven generators installed for peak loads of power. The general adoption of the gas engine, however, made available for purposes other than blowing and power a large surplus of blast-furnace gas which was applied with entire success to the underfiring of coke ovens and to use in the open hearth and in mill heating. The full development of the latter uses is the most important recent advance in heat economy.

The large-scale use of gas for purposes that demanded fine cleaning led to the trial of gas equally well cleaned for stoves and boilers and to a realization of the benefits of such better cleaning. The consequence is that all blast-furnace gas in Germany is given a secondary cleaning and washed gas in the American sense of gas cleaned in scrubbers only does not exist. It is probable that this difference between the usual German practice and that common in America originated from the widespread and permanent adoption of the gas engine in the former country 25 to 30 years ago. In the United States the practically universal use for surplus blast-furnace gas has been in firing the steam boiler, and since fine cleaning of the gas for this purpose was not enforced by the conditions of operation, American development in gas washing has lagged behind. However, conditions of boiler use are now greatly changed, with the result that the value of fine gas for boiler purposes has very greatly increased within the last few years.

The prewar boiler was a relatively simple affair, low in cost and arranged in small units. The modern steelworks boiler embodies all the refinements in steam practice which have been developed as a result of the expansion of public utility installations. The development includes a quadrupling of the average size, a tripling of the steam pressure, the employment of a high degree of superheat and the use of surface condensers with evaporation of the make-up water. Such boilers cost at least \$175 per rated horsepower, and where fired with blast-furnace gas are adapted to continuous service at a high rate of evaporation in every respect but one. It is not uncommon in the steel industry to see a unit of such an installation costing over \$200,000 and equipped for continuous operation so far as its inner surfaces are concerned, which

requires a daily cleaning of burners and a weekly removal of the flue dust deposited on its tubes in order to maintain the rate of efficiency upon which the justification of its cost depends. The elimination of such a condition within a short time may be confidently expected.

Secondary Washing in Germany

The German blast-furnace plant has now for many years included a complete installation for the secondary washing of the entire production of blast-furnace gas with the same regularity that it has included blowing engines and hot-blast stoves. These washing installations are adequate in size and are constructed in accordance with the same generally high standards of engineering which characterize the remainder of the equipment, and they form no small and inconsiderable portion of the blast-furnace plant.

The usual practice is to provide a dry dustcatcher for each furnace and to concentrate all subsequent cleaning equipment into one central installation which handles all the gas produced by the plant. The dry dustcatchers are usually very much larger than corresponding equipment in America and the centralization of gas cleaning results in the erection and use of long gas mains. The total cost of installations of equal capacity varies considerably in accordance with the length of mains, the system of cleaning employed, the character of construction and size of the plant. Excluding dustcatchers and collecting and distributing mains, the cost of a gas-washing plant is at least \$12,500 per hundred tons of pig iron per day. This corresponds to an investment of \$375,000 in a plant of 3000 tons daily capacity.

The operating costs are usually from \$0.00177 to \$0.00283 per 1000 cu. ft. of gas. This corresponds approximately to an operating expense of from \$0.225 to \$0.40 per ton of pig iron. No matter what system of cleaning is employed, there is nothing perfunctory about the gas-washing operation. On the contrary, it is carried on with the same regard to essential details which characterizes the operation of the gas engine. The amount of supervision varies in accordance with the system employed.

In the case of wet washing by the disintegrator method, but little attention is required, aside from the regulation of volume of water employed in accordance with the temperature and quantity of the gas and the temperature of the water. In the case of systems which employ either bag cleaning or electrical precipitation, a very careful regulation of temperature, degree of saturation and of pressures throughout the gas-cleaning system is necessary. All of these requirements are faithfully carried out by thoroughly trained men. This care and operation and the expense which it involves, as well as the size and cost of the

installations, indicate how thoroughly the Continental makers of iron and steel believe in the benefits derived from fine cleaning.

Result of Fine Cleaning

The primary general result obtained through this fine gas cleaning is the ability to refine and control every operation in which the gas is subsequently used. Avoidance of the nuisance and expense of removal of dust from combustion chambers and furnaces in which the gas is burned is secondary. The refinement of all the processes of combustion and use involves other elements than merely the cleaning of the gas, and the remarkable results in the direction of heat economy which have been attained are due to a complete system which includes careful design of furnaces, improved methods of combustion, accurate measurements of pressures and quantities and gas analyses. These refinements are only possible to practice with equipment of which the condition is permanently good, and in which rapid change of conditions due to fouling of apertures, fluxing and disintegration of brickwork and other numerous irregularities which attend the use of partly washed gas do not occur.

Many attempts at refinement of practice under the latter conditions have come to nothing on account of the fact that the semiwashed gas made conditions of operation impossible to control. Operation of the steam boiler in this country may be cited as an example. If such a boiler is equipped with one of the numerous burners which depend for accurate mixing of gas and air on the relative size of orifices, this relative size is disturbed by accumulation of mud in the burners. A regulator provided for the maintenance of a given pressure in the combustion chamber and set for a clean burner works improperly after the burner is fouled. The conductivity of heating surfaces become impaired and the rate of feed and the drop in pressure through the boiler show a progressive variation from the conditions contemplated in the design. The use of preheat for the gas which would otherwise have come into general use many years ago, has proved impracticable on account of the excessive amount of attendance in cleaning required by the preheater and of the progressive reduction in the amount of preheat obtained as the surfaces become coated. Every relation of one part of the system to the other is disturbed and the net loss is many times greater than that represented by the cost of periodical dirt removal from the system.

Where fine cleaning of gas is employed, the situation is exactly the reverse. The mechanical conditions within the system, including size of orifices, conductivity of refractory surfaces, frictional resistance and direction and intensity of gas currents, are constant and the conditions of operation are capable of continuous study and gradual improvement. This study is faithfully and carefully given. The observation and regulation of one condition makes possible the estimation of the value of the

results to be obtained by further regulation. Close study of these conditions in many plants has resulted in a system of operation in which avoidable losses are practically eliminated.

Hot-blast stove operation as often practiced on the Continent is one of many examples that may be cited to show the extent to which regulation and control are practiced. The control apparatus includes flow meters for gas and for air for combustion and for cold blast to the stove. The stove main is held under constant pressure. The chimney draft is automatically regulated. The waste gases are analyzed and the CO₂ as well as the sum of the CO and H in the waste gases are automatically indicated. Under these conditions every variable that can affect the accuracy of the combustion or the degree of heat absorption by the stove is known and the stove efficiency, without allowance for radiation, may be calculated at any time from contemporary data. Under these conditions the waste-gas temperature is often as low as 400° F., the combustion is nearly perfect and the calculated efficiency of the stove without allowance for radiation is about 85 per cent.

The benefit of washed gas is also shown by a practical permanence of the stove construction. In one case a set of stoves has operated for 10 years without repairs, in another, necessary repairs to checkers amounted to 3 ft. of brickwork after three campaigns.

Where gas is used under boilers it is universally cleaned to a point where clogging of surfaces does not occur. Under these conditions and with skillful control, the boiler efficiency is constant and relatively very high. The results include a complete freedom from interruptions on account of either inner or outer tube surfaces.

The large use of gas for driving engines and for underfiring coke ovens permits no argument as to the desirability of gas washing, since both of these uses require gas of the highest possible purity.

Washed Gas in Open-hearth Manufacture of Steel

Another use of washed blast-furnace gas, which is of extreme interest in America, is its application in a mixture with coke-oven gas to the manufacture of open-hearth steel. In several of the best German plants the over-all consumption of fuel in the open hearth is less than 4,000,000 B.t.u. per metric ton of steel. The actual consumption during the busy part of the week when operations are proceeding is from 3,360,000 to 3,600,000 B.t.u. This low rate of use of fuel is accompanied by a remarkable speed in operation. At one plant 70-ton heats made with 70 per cent. scrap and 30 per cent. pig iron are being regularly made in 6 hr. In another plant heats of 180 tons are being made in 8 hr. with 75 per cent. of scrap. The quality of steel at both of these plants is exceptionally good. These results are obtained by a varying proportion in the

mixture of blast-furnace and coke-oven gas, the latter running from 22 to 42 per cent. of the mixture and the B.t.u. per cubic foot from 186 to 279. The higher heat value is used during the period of melting and the lower during the boil and while finishing. The furnace is thus forced when necessary and heat is saved during the time when it is not needed, while at the same time a sufficient volume of products of combustion is available to maintain the proper working pressures within the furnace. This condition cannot be fulfilled while working with straight coke-oven gas without waste of fuel and the ability to introduce a large volume of gas of low calorific power and thus maintain the proper working conditions in the furnace is extremely valuable. Other conditions of operation, including close control, a high degree of regeneration of gas and of air and certain details of the furnace construction contribute to the result. The most important factor, however, is the use at all times of a gas exactly suitable to the temporarily existing conditions.

As applied to mill heating, results equally remarkable with those of the open hearth are being obtained. The consumption of gas in soaking pits used in connection with the rolling of open-hearth steel is about 100 lb. coal equivalent per ton of blooms, and heating operations in continuous furnaces require practically the same amount. These results are obtained in furnaces of good design and under skillful operation. The remarkable results, however, are due largely to the use of a carefully predetermined mixture of coke-oven gas with fine cleaned blast-furnace gas.

The situation of the iron and steel industry in Germany after the war was one that required the utmost possible effort in the direction of economical use of resources. The circumstances of shortage of working capital combined with slack demand led to an intensive study of all conditions affecting the use of fuel and the adoption of the best possible means for its realization.

As a result of this intensive study of available means for the better application of by-product gases and of waste heat from gas engines, there are several plants in Germany in which no coal excepting that used at the coke oven is employed for mill purposes, including transportation within the works. An exception to this is to be noted in the case of narrow-gage locomotives operating within the steelworks buildings where for reasons of convenience and safety steam is still employed. The possibility of completely avoiding the use of coal is based in part on the manufacture of steel by the basic Bessemer process. It is, nevertheless, a very remarkable achievement in thermal economy. The results have been particularly notable within the last five years, within which time the consumption of coal for auxiliary purposes has within these works been reduced from 1100 lb. per ton of finished product to practically nothing. The total estimated saving to the German steel industry produced by the

adoption of better methods of fuel use is 200,000,000 gold marks per year. These economies may be said to have been produced almost entirely by more skillful methods in the use of blast-furnace and coke-oven gas, the use of the blast-furnace gas requiring in every case a secondary washing.

Standard of Cleanliness in German Practice

The standard of cleanliness in German practice permits a maximum content of dust in gas of 0.04 grains per cu. ft. of gas. This corresponds to the limit of cleaning possible with the fan installations which are still used on a considerable scale for the washing of gas for stoves, boilers and heating furnaces. A higher degree of cleanliness is considered preferable even by those operators who are continuing to use the fans. However, in Germany, as elsewhere, an installation once made is difficult to replace so long as operation is possible with the existing facility. Gas cleaned either by the disintegrator or the Halberger-Beth system of bag filters may be brought to 0.002 grains per cu. ft. The degree of cleanliness is fixed in the case of the bag system. With the disintegrator the degree of cleanliness may vary from the figure given above up to 0.009 in accordance with the method of operation. Fine gas, as understood in Germany, has a content of dust below this latter figure. Standard practice requires the best cleaning of which the disintegrator or the Halberger-Beth apparatus is capable where the gas is to be used in engines or in coke-oven underfiring. There is a very strong disposition to insist on an equal degree of cleanliness for gas used in open hearths and in mill heating. Progressive operators are practically unanimous in the opinion that cleaning to a degree of fineness higher than 0.009 is not economical in view of the fact that the cost of the finer washing by the disintegrator may now be reduced to a figure practically the same as that of the less perfect cleaning accomplished by the older fan installations, which still have a very considerable use.

German Systems of Gas Washing

It is natural that a progressive industry should have developed more than one system of gas washing. The first completely successful method developed for use in connection with the gas engine included precoolers or scrubbers in the shape of towers partly filled with wooden grillwork and sprayed with water. Secondary cleaning was performed in the so-called drum-type Theisen washer. The tower scrubber remains as an essential part of all wet-washing systems. It is also used as an after-cooler in connection with the bag filter system in order to reduce the temperature of the gas and so lower the maximum possible content of water vapor. In connection with the electrical precipitation system,

generally the scrubbing tower will be used both before and after the precipitator, although the occasion for its use will depend on local circumstances with regard to the distance over which it is necessary to transport the gas.

The scrubber as used in Germany is characterized by many variations of detail. These include the extent and location of wooden grillwork and the method of applying the spray. There is a disposition to locate the water sprays on the flat upper surface of the tower, as is sometimes done in American benzol scrubbers. Generally speaking, the development of the cooling tower has been similar to the corresponding development in America and I know of no particular with regard to which the European scrubber is better than the American; in fact, the approved type of American scrubber probably effects a more intimate mixture of gas and water than do the scrubbers usually employed in Europe. This is natural, since the content of dust in the gas issuing from the scrubber is less vital in Europe than in America, where the scrubber has for most purposes constituted the entire washing system. Tower scrubbers equipped with rotating parts for the finer spraying of the water are not used in Europe, although the Feld washer, of which numerous American installations have been made in recent years, is a European development. Continental practice, however, prefers the installation of rotating elements or other mechanical devices within a secondary washer.

For purposes of fine cleaning the disintegrator came into general use as a secondary washer many years ago. For new installations it almost completely replaced the drum-type Theisen and the water-sprayed fan, although the latter continues to be used in many locations. The construction of the drum-type Theisen is well known in America, in view of its practically universal adoption in American gas-engine installations.

Uses and Types of Disintegrators

The disintegrator is a type of apparatus originally applied to the fine crushing of coal and other materials, a purpose for which it had a very considerable development and which in some degree still continues. It consists essentially of a shell similar to the casing of a fan and provided with a rotating shaft on which is mounted a disk either centrally or at one side near the casing. The disk carries successive circular rows of bars which rotate rapidly between corresponding circular rows of bars fixed to the casing. The system is arranged to be sprayed with water in a fine state of division, the spray proceeding from points near the rotating shaft. The fine water spray is thrown uniformly into the space occupied by the rotating and stationary bars through which the gas is required to pass. The result is a complete wetting of the smallest particles of dust and the formation of globules of water of which the dust

particles form the nuclei, these globules being large and heavy enough so that their subsequent elimination from the stream of gas is easy.

The disintegrator now is practically always preceded by a spray tower for cooling, although installations have been made in which the entire washing was performed within the disintegrator. This practice is extremely uneconomical on account of the fact that the water necessary to cool and clean the gas is approximately four times that required for cleaning alone. The horsepower depends almost entirely on the amount of water used within the machine, and there is an upper limit of water circulation beyond which the use of power becomes prohibitive. Under these circumstances the capacity of the disintegrator without previous cooling is about 25 per cent. of that possible when precooling is practiced. These circumstances have led to the practical abandonment of systems in which the entire cooling and washing process was carried on within the disintegrator.

Various types of disintegrator have been successfully used. The basic principles are similar, consisting in the passage of a mixture of gas and water between rapidly rotating and stationary bars. The total number of bars may be four or six. They may be of any desired cross-section and many variations in their shape were made in former years. The preferred construction now is the use of round bars as fixed members and of angle irons or "T" bars for the rotating elements. The clearances are quite close and the speed of rotation is practically as rapid as is consistent with a correct factor of safety in the design. An exception to this is found in the Schwartz-Bayer construction, in which the two rows of bars rotate in opposite directions in separate cages instead of having one system of bars fixed. In this case the speed necessary to produce the same washing effect is one-half of the other. The construction, however, involves a double drive and the carrying of the disintegrator proper on overhung shafts excepting as a telescopic shaft may be employed. Fine cleaning may be effected with the gas entering at the center and leaving at the periphery, or vice versa. The Theisen disintegrator employs the former method and the Schwartz-Bayer type the latter. The Theisen design also incorporates a fan in the disintegrator construction, the fan blades being located outside the circle of the disintegrator proper. This fan element is used to overcome the loss of pressure in the machine and to create a further pressure for delivery to the point of use. In the case of the Theisen disintegrator the water is fed into a perforated revolving drum which surrounds the shaft, the water issuing from the perforations and striking the rotating bars of the disintegrator.

Variations in the details of design of the disintegrator have been made as a means of reducing the power consumption where extremely fine cleaning was not required. These include reduction in the number of circles of rotating and stationary elements from six to four, and also the

TABLE I.—*Experimental Operation of Disintegrator with Varying Amounts of Water and of Gas*

Duration of Test	Gas Quantity, Cu. Ft. per Min.	Cooling Tower Water		Disintegrator		Water to Tower and Disintegrator		Temperature of Gas		Kw. per M. Cu. Ft. Gas, per Min.	Gal. Water to Disinteg- rator, per Min.	Kw. Used Disinte- grator			
		Dust Content		Dust After Cooling Tower		Dust After Disintegrator		Tower							
		After	Before	Grains per Cu. Ft.	Gas	Grains per Cu. Ft.	Gas	Before, Deg. F.	After, Deg. F.						
Aug. 2-21.....	35,314	850	24.08	0.35	7.54	0.0012	31.62	240	About	11.74	266	415			
Aug. 23-30.....	41,200	934	22.68	0.29	6.37	0.0014	29.03	to	68	9.81	262	404			
Sept. 23-24.....	50,028	1,010	20.20	0.36	4.03	0.0022	24.23	to	to	7.22	209	361			
Sept. 27-Oct. 5.....	52,971	1,082	20.42	0.33	4.22	0.0038	24.64	356	72	6.85	224	363			
Oct. 6-11.....	58,857	1,291	21.93	0.31	3.81	0.0044	25.74			5.85	224	344			

elimination of the stationary elements. These are practicable methods of producing the desired result. Recent development, however, is in the direction of increasing the gas flow through the disintegrator without varying the amount of water fed to the machine, as a means of reducing both the power and water consumption of the operation. The water supply is maintained practically constant and the use of power varies almost exactly as the water. The demand for power by the disintegrator proper is almost entirely independent of the amount of gas which passes through the machine, although there is some increase in the power required by the fan with higher rates of delivery of gas.

The change in method, therefore, consists merely in the operation of the disintegrator beyond its rated capacity. The loss in fineness of cleaning is comparatively slight and the disintegrator is capable of operation at a capacity of 60 per cent. or more beyond that for which it is designed when the finest possible cleaning is desired. At this 60 per cent. overload rating, the degree of cleanliness is well below that possible in secondary washers of the fan type. A statement of the circumstances of operation under various conditions of load is shown in Table 1.

These figures indicate the possibility of sufficiently fine cleaning for all uses excepting gas engines and coke underfiring with a very greatly lessened consumption of power as compared with that formerly considered necessary for disintegrator operation. It should also be noted that the power given for maximum output of gas compares with about 6.6 kw., where the fan system of cleaning is employed, the degree of cleanliness in the latter case being 0.04 gr. per cubic foot.

Wet Washing Methods

Mechanical wet cleaning by either the disintegrator or the fan method involves the provision of a water separator after the mechanical washer. In Germany this separator usually takes the form of a chamber provided at the bottom with a water seal and containing a system of inclined baffles against which entrained particles of moisture may strike. This results in the aggregation of finer particles into large drops and the elimination of water by running down the inclined surfaces of the baffles. These separators are either rectangular or circular in cross-section and for a disintegrator of 35,000 cu. ft. per min. will have a diameter of about 9 ft., and a height of 18 or 20 feet.

The wet-washing method involves the disposal of the dirt removed from the gas as sludge and several variations in method of accomplishing this separation are practiced. At one plant a system of air pumps and tanks is employed, the sludge combined with the proper proportion of water being sucked into the tanks under vacuum and afterwards ejected

through the delivery pipe by pressure. At another plant the water is clarified by treatment with milk of lime and subsequent subsidence. This lime is mixed with the gas washer effluent by means of an undershot water wheel which operates a system of small buckets, these buckets rotating on the same shaft which carries the water wheel and successively dipping into the lime solution and at the proper point in the circle of rotation ejecting it into the stream of gas-washer water. The lime feed is thus maintained proportional to the amount of gas-washer effluent. At this plant, where 175,000,000 cu. ft. of gas per day are cleaned, the consumption of lime is 11,000 lb. per day. The clarification of the water for all industrial purposes is complete. The dust settles to the bottom of the settling basins, of which two are provided in order to permit alternate cleaning. Subsequent removal is by means of a pump with disposition by means of freight cars to the dump. Other settling-basin installations employ grab buckets for cleaning the compartments of the system after subsidence of the dust and drainage of the water. Generally speaking, I would say that none of these systems is equal in convenience and overall cheapness of operation to the combination of the Dorr thickener and the vacuum filter now used in America.

Apparently there is no attempt to sinter or otherwise treat the dust from the washer for further metallurgical use. The dust is, generally speaking, low in iron content and in some cases contains considerable proportions of lead and zinc which are undesirable for further use. The sludge is therefore either stock-piled with a view to possible future use, or it is put over the dump. In some cases it is used after two or three years in the stock pile for back filling of the coal mines in order to prevent subsidence of the surface.

An alternative to the use of the disintegrator in mechanical wet cleaning is the use of the fan as designed and manufactured by Zschokke and Dinnendahl. The apparatus in this case is exactly what its name suggests—a double-entry fan. Adaptation to gas washing is effected by the inclusion in the construction of a turbine wheel mounted on the shaft and located in each gas inlet. The outside of these wheels is open and a feed pipe enters the fan just below the shaft and discharges into the turbine wheel. The opening between the blades of the turbine is set at an angle to the axis of rotation, so that the water is projected into the fan with the stream of entering gas. The current requirement per thousand feet of gas per minute is about 6.6 kw. The water requirement is somewhat greater than that of the disintegrator and the limit of cleanliness of the gas is 0.04 gr. per cu. ft. At the most progressive plants the disintegrator is therefore preferred. The other elements in the wet-washing system where the fan is employed are exactly the same as where the disintegrator is used and consist of precooler, fan, water eliminator and provisions for sludge disposal.

Halberger-Beth System

An alternative to the wet cleaning method, and one which has been practiced on a very considerable scale in Germany for many years, is the Halberger-Beth system of bag cleaning. This system, as the name indicates, was developed by the Halberger-Huette and was taken over and manufactured by Zschokke, who has also developed the fan system of wet-cleaning the filter. The unit of a Halberger-Beth plant consists essentially of a rectangular chamber in which bags of cotton fabric are stretched on frames so as to form a complete mechanical filter for the gas. As usually constructed, the bag filters are arranged in two rows, one on either side of the chamber, with about 12 pairs of bags making up the unit. This arrangement is made in order to facilitate the periodical cleaning of the filters, which is necessarily practiced. The capacity of one chamber is about 20,000 cu. ft. of gas per min. The gas enters the chamber and is forced from the outside of the bags to the inside. Each bag has a separate outlet pipe into a common header for washed gas, the header being located above the cleaning chamber on a line with the long axis. The bottom of the chamber is divided into two bins, one under each row of bags, the intersection of the bin slopes being parallel to the long axis of the chamber. In each of these troughs is located a screw conveyor by means of which the dust is conveyed to a separate bin beneath.

The system necessarily includes a set of mechanical hammers, one for each bag and a secondary system of piping through which a small percentage of purified gas is delivered to the inside of the bags and forced through the fabric in the reverse direction from the ordinary flow for the purposes of cleaning the filter. This percentage of gas is about 6 to 10. The reversal of flow for periodical cleaning is automatically effected, so that each bag is cleaned and hammered in turn. The mechanical means for accomplishing this cleaning are beautifully worked out and are entirely automatic. A system of shafts mounted on either side of the cleaning chamber successively closes the exit valve from the bag to the cleaned gas header, opens the valve for reversed flow of purging gas and operates the hammer. After this cleaning has proceeded for a few seconds, the hammering ceases and the valves are again reversed. These mechanical features are thoroughly reliable and cause little trouble or expense. The general circumstances of operation, however, require very close observation and control. The temperature of the gas must be below 100° C., this temperature being the upper limit to which the bags may be exposed without rapid deterioration. On the other hand, the gas must be kept above the dew point, which is usually about 50° C., and the operation must be carried on between these limits. The long mains of large diameter which carry the gas to the central cleaning plant have a very considerable cooling effect, and at many plants it is possible during much of the year to cool to the proper

temperature without special means. However, the system necessarily includes a system of tubes contained within a tower on the inlet side of the system. These tubes may be used to carry low-pressure steam for heating the gas or cooling water for reducing its temperature. On the outlet side of the cleaning system an aftercooling tower, quite similar to those employed in wet washing, is usually located in order to reduce the temperature of the gas to a point at which moisture will not drop out in the pipe or at the burner.

The drop of pressure through the bag system is very considerable. As the plants are usually constructed, it amounts to 4 in. of water. The system always includes large fans which are placed on the outlet side of the cleaning system so as to take advantage of the cleanliness of the gas. Avoidance of a vacuum within the system therefore requires a pressure from the furnace top, which is sufficient to give 4 in. of water at the filters, or the operation of the filtering chamber under a vacuum. These chambers are provided with doors opposite each bag in order to facilitate the renewal of the filters, and under conditions of vacuum these doors must be kept absolutely airtight in order to avoid mixtures of air and blast-furnace gas. In every case the installation includes a complete set of pressure gages for observation throughout the system registering within the fan room. The danger of a vacuum in the system may be obviated by the reduction in speed of fans, by decreasing the number in operation or by throttling the outlets. This procedure may be so conducted that a sufficient pressure will be created on the inlet side to force the gas through the filter and such a system of control seems absolutely necessary for safe operation. However, occasional operation with a vacuum in the system seems to be not unusual in some German plants.

The power requirement for the Halberger-Beth system is about 1.5 kw. per 1000 cu. ft. of gas per min. for the fans and 1.2 kw. for all other purposes, the total being 2.7 kw. per 1000 cu. ft. of gas per minute.

The fineness of cleaning with the Halberger-Beth system is very good. It is probable that the average of results produced are somewhat better with this system than with the disintegrator, although inspection of operating records shows that this is not necessarily the case. The cost of the Halberger-Beth system is higher than with the disintegrator and the amount and skill of supervision required is also greater. The system has been in use for many years and is well regarded.

Electrical Precipitation

The newest method of gas purification, and one that is exciting a very considerable interest on the part of all German iron and steel men, is the electrical precipitation system. This is based on the American patents of Cottrell and on the contemporaneous work of Mueller. At the present time it is being pushed by two separate organizations, the

Siemens-Schuckert Co. and the Elga Electric Gas Cleaning Co. The former is well known as one of the largest and most successful German manufacturers of electrical equipment. The Elga company was formed by a combination of Zschokke and Dillingen. An experimental plant for the development of the electrical system was built several years ago at the latter place. Much of the development of the Siemens-Schuckert system was obtained at Dortmunder Union, where an experimental plant was constructed in 1923. At the present time the largest electrical gas-cleaning plant in operation is that at Witkowitz in Czechoslovakia, which was installed by Elga. This plant has a capacity of 35,000 cu. ft. of gas per min. and an extension of the same size is nearing completion. The largest plant under construction is that now being built by Elga for Mannesman A. G. This plant is to have a capacity of 162,000 cu. ft. of gas per min. Two other smaller plants are also under construction by Elga. Siemens-Schuckert is constructing a plant with capacity of 118,000 cu. ft. per min., for the new Krupp works at Berge-Borbeck, together with four smaller plants.

The underlying principles of electrical precipitation are well understood in America, and the system was several years ago applied at Dunbar, Pa., its most recent application having been at the plant of the Colorado Fuel & Iron Co. Neither Siemens-Schuckert nor Elga have made any radical or revolutionary change in the original principles as developed by Cottrell and Mueller. Much careful study of details both with respect to the electrical conditions and to the difficulties resulting from the composition of the gas has been done. This study has not resulted in complete agreement between the two companies as to the conditions necessary to fulfill, nor as to the preferable means to be employed. Both companies require a temperature in the gas below 100°. This is necessary in order to make certain that all vapors of silica and other slag-making materials formed in the furnace are condensed. Elga also embodies in its system a requirement as to relative humidity of the gas on account of the greater electrical resistivity of gas as it approaches the point of saturation. The Siemens-Schuckert idea is that the separation may be effected independently of the degree of saturation of the gas. Elga has also embodied in its plant at Witkowitz the idea of cleaning the system by means of purge gas, which has been described in referring to the Halberger-Beth system. An inclination toward this procedure probably arises from the previous experience of the company with that system. The Elga purifier, therefore, stops the flow of uncleaned gas in each section of the precipitator in turn, shuts off the current and reverses the direction of flow of gas, using previously purified gas as means for cleaning. Siemens-Schuckert propose a continuous use of the compartments with no reversal of flow. Both systems, however, include mechanical hammers automatically operated as means of cleaning. It

therefore appears that the Siemens-Schuckert system if equally successful in effecting purification is preferable to the Elga with respect to the use of purified gas for cleaning and with respect to the necessity of maintaining a definite condition of relative humidity. These differences will result in a much simpler and cheaper operation in the case of the Siemens-Schuckert. A complete knowledge as to the correctness of these conflicting ideas is as yet lacking.

It is interesting to note the difference in construction whereby Siemens-Schuckert propose to eliminate the complications just referred to as applying to the Elga. The latter company employ a tubular construction, the cleaning unit being a vertical pipe about 6 in. dia. and containing a single positive electrode running through its center. The voltage of the Elga is 40,000.

On the other hand, the Siemens-Schuckert employs a rectangular compartment in which the positive electrode consists of a section of wire mesh extending practically across the compartment. The electrode surface in proportion to the total volume within the compartment is therefore greater than is the case with the Elga. The proposed voltage for the Siemens-Schuckert installation is 60,000. Furthermore, the Siemens-Schuckert system contemplates two passes for the gas within the electric field, entry being at the top of a primary compartment which is connected to a secondary compartment at the bottom, the gas traveling downward in the primary and upward in the secondary and being exposed to the electrical action in both compartments. The total travel of the gas within the electric field is about 30 ft. in the Siemens-Schuckert system and about 11 ft. in the Elga. The proposed velocity of the gas in the two systems is not sufficiently different to result in an equal time exposure of the gas, a maximum velocity of about 10 ft. per sec. being contemplated in both cases.

Precipitation Plant at Witkowitz

The present plant at Witkowitz consists essentially of a long rectangular chamber in shape exactly similar to that used for the Halberger-Beth. The individual units of the electrical precipitators are disposed in this chamber in two rows; each unit is composed of seven vertical pipes forming a cluster, and each cluster is contained within a rectangular compartment built of plate work. Raw gas conduits are provided on either side of the chamber near the bottom. The gas enters from these conduits and rises in the pipes, proceeding thence to pure-gas conduits parallel to and located above the raw-gas conduits. Between each unit and the cleaned-gas conduit is a valve provided with means for automatic opening and closing. Cleaned gas is also piped along on both sides of the system and distributed by means of a separate pipe entering each cleaning compartment. Each unit is also provided with automatic

mechanical hammers and an automatic switch for shutting off the electrical current. The cleaning operation is carried on automatically, each compartment being treated in turn. The current is switched off, the valves reversed so that the normal flow ceases and pure gas enters the compartment in the reverse direction, while at the same time the pipe assembly is pounded by the mechanical hammers. The percentage of gas used for purification runs from 10 to 12.

Auxiliary features of the installation include a precooler for the gas, similar to an ordinary small spray tower. In this tower the purpose is to cool and humidify the gas without precipitation of moisture. The means of water distribution are not sufficiently good to make this attempt successful. About 60 per cent. of the water sprayed is absorbed into the gas and the other 40 per cent. is withdrawn at the bottom of the tower. The gas is cooled to about 70° C. in the precooler. On entering it contains 30 to 35 gr. water vapor per cu. ft.; about 9 gr. more water is added in the tower. This amount of water is not considered sufficient, and at the present time a small portable boiler is employed to make additional steam, which is discharged into the gas main ahead of the purifier. Six grains more per cubic foot are added by the boiler. With the electric system of purification it is of the utmost importance to prevent the dropping of the temperature of the gas below the dew point. In the Halberger-Beth system this results in deposition of mud upon the filters, a condition which would become serious if it persisted for any length of time but which momentarily causes no damage. The condensation of water vapor upon the insulators of the electric installation will cause a short-circuiting which puts the entire system out of operation. The likelihood of such an event is increased by the necessity of operating with the gas 85 to 90 per cent. saturated with water vapor. In order to avoid the possibility of condensation, a heater is provided for the reheating of the purge gas subsequently used in purification. This heater resembles a vertical tubular boiler and is supplied with fuel in the shape of clean blast-furnace gas, the daily consumption being 175,000 cu. ft. The observed rate of use of current for operation at the rate of 27,000 cu. ft. of gas per min. was 7 kw. The drop in pressure through the cleaners is 1.6 in. The purified gas is taken directly in a long main to the stoves, the gas engines on the plant being still supplied with gas cleaned by a disintegrator. A very considerable amount of water drops out in this pipe, but in view of the fact that it is practically clean, no inconvenience is caused. The walls of the combustion chamber were perfectly clean and the gas flame showed the blue color that characterizes perfectly clean gas, with none of the pink tinge that results from the presence of impurities. This difference in color of flame is employed in the purifying plant as a means of control. The degree of cleanliness is 0.01 gr. of dust per cubic foot.

The new construction at Witkowitz varies from the plant at present in operation only with respect to the arrangement of the tubes in each section. The new plant proposes a section composed of 20 tubes instead of seven. In other respects the construction is practically the same.

No large plant of Siemens-Schuckert type is as yet in operation. The company has, however, given a positive guarantee to bring the gas down to 0.004 gr. per cu. ft. and operating experience based on the performance of this plant will be available within a few months.

Dry Separation of Dust Prior to Wet Washing

In addition to the interest at present displayed in electrical precipitation there is also a considerable activity in the development of methods of dry separation of dust prior to wet washing. The most promising of these attempts appears to be in the apparatus now under construction in large German works which proposes centrifugal separation in a plurality of parallel horizontal pipes about 18 in. dia., within which the gas is given a whirling motion by means of stationary screws. These pipes open on the lower side into a chamber without inlet or outlet excepting for dust removal, the gas being carried through the chamber within the pipes. This installation will shortly be in operation.

Cost of Gas Cleaning in Europe

The average cost of cleaning by any of these systems varies in accordance with local circumstances, including the cost of labor, of water and of power. Available figures indicate that the cost with the wet method averages about \$0.00177 per 1000 cu. ft. of gas per min. With the Halberger-Beth system the average cost is probably about \$0.00283 per 1000 cu. ft., although in one case a figure as low as \$0.00169 was taken from the company's records. The cost at Witkowitz was stated to be \$0.00146 per 1000 cu. ft. This cost would be increased to about \$0.0021 by reducing the output sufficiently to permit the production of engine gas. These figures will probably be increased by about 30 per cent. for operation in America under the same conditions.

Costs of plant are difficult to compare on account of other variations in the construction, aside from the gas-cleaning system itself. The cost of the Halberger-Beth system is probably 40 per cent. greater than that of wet washing with the disintegrator. The cost of the electrical system will be somewhat less than that of the Halberger-Beth on account of the greater amount of gas handled per unit.

APPLICATION OF GAS WASHING IN AMERICA

Interest in gas washing in the United States is very properly directed first to its economic aspect and second to its means of application. The

question in the minds of responsible Americans is, "Will fine cleaning of blast-furnace gas pay?" The answer is most decidedly in the affirmative. It must, however, be understood that the expectation of profit through gas washing must be based on the fulfillment of all the conditions of economical use. Of these, fine cleaning is the first. It must, however, be emphasized that the fine cleaning of gas is part of a system of heat economy which includes skillful allocation of the gas in accordance with its nature and the character of the uses to which it may be applied. The system also involves adequate furnaces of good design, the proper means of combustion and close control. Blast-furnace gas has a nominal heat value of approximately \$1.90 per ton of pig iron, based on an average price of \$3.75 for coal including cost of firing. After cleaning, the freedom from nuisance, ease of transportation and control and avoidance of expense for gasification or firing make it worth considerably more than its nominal heating value plus the cost of cleaning. In its uncleared condition it is worth very considerably less than this amount.

Practically all of the recent American advances in metallurgy have been closely connected with the better preparation of raw materials and of fuel. Our ores are now very closely graded, our coking coals are selected in accordance with their character and brought from great distances in order to produce a mixture exactly suitable for use. Our steelmaking processes are now based on a substantially uniform character of pig iron, the specifications for which correspond exactly to metallurgical requirements. The more complex rolling and fabricating processes are entirely dependent on a correct quality of steel. Of all the important materials which enter into steel production on a large scale, blast-furnace gas has been most neglected with respect to preparation and intelligent use. Fine washing of this gas may be expected to produce results as profoundly important and as far-reaching in proportion to the value of the materials involved as has the grading of ores and the selection and classification of coals. These two latter processes of selection and preparation have made possible the results commonly attained by the by-product coke oven as now constructed and in the modern blast furnace.

The present tendency is to increase the care exercised in the preparation of ore and of coal and no one for a moment would consider the abandonment of any of the precautions now taken with respect to the preparation of these materials. Once the corresponding preparation has been practiced with respect to blast-furnace gas and the benefits of its use in properly designed apparatus have been realized, there will be an equally strong realization of the folly of returning to the methods of preparation generally heretofore practiced in America. The reduction in operating expense possible through the proper application of washed blast-furnace gas remains the most important single unrealized means of reducing the cost of American steel.

With regard to the technical means to be employed in the proper preparation of gas, it is probable that the broad experience that will be gained in the near future in electrical precipitation in Germany will lead to a considerable application of this method in the United States. It seems probable, however, that it will be necessary for this development to demonstrate that cleaning may be carried out in a straightaway process without the use of 10 per cent. of the gas for purification of the system and without the complications resulting from the necessity of extremely close control of temperature and humidity as now practiced in the Elga system. The development of gas cleaning under a system which proposes freedom from these complications as yet has been on a scale that is little more than experimental. The financial and technical strength of the developing company and the positive guarantees they have given with regard to the plants now under construction indicate a strong probability of successful operation of electrical-precipitation plants under circumstances that will be interesting in America.

In the meantime, wet cleaning by the disintegrator method remains the simplest, cheapest and most flexible of the thoroughly tried systems developed by Continental experience. Recent developments in Germany make possible a substantial reduction in the power and water consumption of the disintegrator when cleaning for many purposes and a still further reduction in power may be made by the separation of the fan from the disintegrator proper, and in many cases by its entire elimination with propulsion of gas by the blowing engines. Recent American developments in dry cleaning will make possible the reduction in cost of disposal of the sludge attendant upon wet washing. This cost is practically proportional to the amount of dust removed in the wet system rather than on the amount of gas handled. The preliminary removal of a large percentage of the dust by dry methods will not only effect a substantial reduction in the cost of wet washing but will enable a classification of flue dust into dry and wet, which can be made to correspond to the degree of fineness above which sintering of the dust is possible by present methods. Wet cleaning by the use of the disintegrator may therefore be expected to have a continued use irrespective of the development of the electric precipitator. It is also probable that the increasing American interest in fine gas cleaning will result in modifications of present plant and practice which will still further reduce the cost. As practiced in Germany, however, the science and art of gas cleaning has been sufficiently developed to form an entirely sound basis for American installations and the American industry can proceed rapidly to a realization of the important heat economies possible through the application of washed gas as they have been described in this paper.

DISCUSSION

R. FRANCHOT, Washington, D. C.—The author says that it is "to be noted that solid fuel is more economical and capable of giving a higher boiler efficiency, as well as a greater production from the same boiler, than is blast-furnace gas." That statement brings up the general question as to the economy of the present trend of blast-furnace practice, which I think is generally recognized to show a definite tendency toward a primary use of the furnace as gas producer, with pig iron as a by-product.

Mr. Brassert, in his paper¹ before the Bituminous Coal Conference in Pittsburgh in the fall of 1926, stated unequivocally that the blast furnace should be run with its greatest efficiency in iron making and that it was uneconomical to use the blast furnace as gas producer. This point raises the question as to how much difference there is in the efficiency of solid fuel (in boilers particularly) and blast-furnace gas, and I would like to ask the author if that difference is substantial. If, for example—this may be an extreme case, I am not sufficiently familiar with the subject—the difference were 50 per cent.; that is, suppose that the blast-furnace rejection in its top gas, roughly speaking, is half of the energy of the coke. If the use of that gas is half as efficient as that of other fuels, 25 per cent. of the coke charged into the blast furnace is being thrown away.

C. W. ANDREWS, Chicago, Ill.—I believe that Mr. Boynton is trying to bring out the fact that with modern steam-power plants using powdered coal the labor cost is low, and the boiler plant is able to take care of high overloads, which is not the case with blast-furnace gas at present. Coal for a boiler can be of the lowest grade, especially if it is powdered, but for producer plants a better grade of coal is needed, which is going to cost considerably more. Consequently, if the producer can be eliminated by using gas fuel, which already is available, expense will be saved in the plant as a whole.

R. FRANCHOT.—Of course there can be no question as to the economy of using blast-furnace gas if it is made. My question is how much better economy it would be not to make it. I wonder if Mr. Andrews could give an estimate of the difference in the actual efficiency of blast-furnace gas as compared with powdered coal?

C. W. ANDREWS.—That question is pretty hard to answer. I do not feel qualified to give such an estimate. Mr. Franchot is bringing out, and quite properly, what Mr. Brassert emphasized last year; namely, that the blast furnace should be used as a pig-iron producer. There is no reason for argument until we get to the point where we can decrease the gas in order to make better or cheaper pig iron. So long as we have the gas, let us use it where it will mean the greatest economy to the plant as a whole.

¹ H. A. Brassert: Possibilities of Fuel Economy in the Iron and Steel Industry. *Proc. Internat'l. Conf. on Bituminous Coal.* Carnegie Inst. Tech.

Operation of Blast-furnace Plant of Columbia Steel Corp. at Ironton, Utah

By W. R. PHIBBS,* PROVO, UTAH

(New York Meeting, February, 1928)

THE blast furnace of the Columbia Steel Corp., at Ironton, Utah, was put in blast April 30, 1924, and its operation has presented some interesting problems. The coke for the furnace is furnished by 33 Koppers Becker type ovens of 15 tons capacity each. The coal is shipped from the company's mine at Columbia, Utah, which is approximately 123 miles from Ironton, and is probably the highest volatile coal that is being coked for blast furnace use in this country. The analysis of the coal is:

	PER CENT.
Moisture.....	3.90
Volatile.....	39.00
Fixed carbon.....	51.10
Ash.....	6.00
Sulfur.....	1.07

The analysis of the coke is:

	PER CENT.
Volatile.....	0.55
Fixed carbon.....	89.70
Ash.....	9.75
Sulfur.....	1.05

The coke is light and of a fingery construction, but is very fast burning. A screen test of the coke as loaded into the skip tubs at the furnace shows the following:

	PER CENT.
On 2 in.....	17.90
On 1½ in.....	41.78
On 1 in.....	27.80
Through 1 in.....	12.52

The by-product yields are as follows:

Gas.....	11,000 cu. ft. per ton of coal
Sulfate.....	30 lb. per ton of coal
Tar.....	12.65 gal. per ton of coal
Motor fuel.....	3.00 gal. per ton of coal
Average B. t. u. in gas.....	567

* General Superintendent, Columbia Steel Corpn.

The ore for the blast furnace is shipped from Desert Mound, Utah, near Cedar City, in the southern part of the state. The mine is approximately 231 miles from Ironton. The ore is a hematite, disseminated with magnetite, and the chemical analysis shows approximately 12 to 20 per cent. magnetite, although under a microscope the ore has the appearance of a magnetite. Having only one grade of ore, the problem has been to prepare and handle this ore to the best advantage. The ore, being very dense, is crushed and screened. At present it is screened to three sizes, $\frac{3}{4}$ in. and under, $1\frac{1}{2}$ in. and under, and over $1\frac{1}{2}$ in. The maximum size of the over $1\frac{1}{2}$ in. is approximately 2 in. The ore is shipped to the plant the year around. In crushing and screening the ore to the three grades, the analysis of each grade is different. The iron content is higher in the coarse ore, and the silica is higher in the fine ore. When the ore is received at the plant it is grouped according to analysis. The following is an average analysis of the ore, on a natural basis:

	PER CENT.
Fe.....	53.0
Mn.....	0.09
P.....	0.18
SiO ₂	8.5
Al ₂ O ₃	2.75
CaO.....	1.20
MgO.....	2.75

From the beginning of the furnace operation, April 30, 1924, to March, 1925, the ore was crushed but not screened, and was graded according to silica content as follows:

First grade.....	7.0 per cent. and under SiO ₂
Second grade.....	7.0 to 9.0 per cent. SiO ₂
Third grade.....	9.0 to 11.0 per cent. SiO ₂

The ore was charged into the furnace as follows: One round first grade, one round second grade, one round third grade. A screen test of the ore was as follows:

	PER CENT.
On 1 in.....	56.6
On $\frac{3}{4}$ in.....	6.9
On $\frac{1}{2}$ in.....	8.3
On $\frac{1}{4}$ in.....	10.8
Through $\frac{1}{4}$ in.....	17.4

The coke consumption on basic and foundry iron for this period was as follows:

COKE PER TON OF IRON

	Foundry, Lb.	Basic, Lb.
Per period.....	2713	2457

From March, 1925, to February, 1926, the ore was graded according to size. Two sizes were used and charged according to a layer method of filling. Each charge contained either fine or coarse ore, and was charged as follows: coarse ore, fine ore, coarse ore, fine ore, etc. The screen test of the ore during this period was as follows:

	PER CENT.
On 3 in.....	2.5
On 2½ in.....	4.2
On 2 in.....	17.5
Through 2 in.....	75.8

The ore was screened over a $\frac{3}{4}$ -in. screen, which produced a product of 50 per cent. fine ore, and 50 per cent. coarse ore. During this period the coke consumption was as follows:

COKE PER TON OF IRON

	Foundry, Lb.	Basic, Lb.
Per period.....	2402	2122

During February, March and April, 1926, a mixed filling was employed of two sizes. Each charge contained coarse ore and fine ore, mixed in the skip tubs. Starting Feb. 15, 1926, the coarse ore over 1 $\frac{1}{2}$ in. size was recrushed to the following sizes:

	PER CENT.
On 1½ in.....	5.0
On 1 in.....	15.0
On $\frac{3}{4}$ in.....	25.0
Through $\frac{3}{4}$ in.....	55.0

Coke consumption during this period was as follows:

COKE PER TON OF IRON

	Foundry, Lb.	Basic, Lb.
Per period.....	2398	2291

From May, 1926, to March, 1927, three sizes of ore were charged into the furnace. The different sizes were charged in layers, that is, each charge contained one size. The filling was approximately as follows: fine ore, coarse ore, fine ore, medium ore, and the screening size was as previously described. For this period the coke consumption was as follows:

COKE PER TON OF IRON

	Foundry, Lb.	Basic, Lb.
Per period.....	2289	2067

From March to December, 1927, the sizing of the ore and filling was the same as during the above period, except that a blank of fine ore was employed at regular intervals, with the result that the coke consumption for the period was as follows:

COKE PER TON OF IRON		
	Foundry, Lb.	Basic, Lb.
Per period.....	2111	1851

The results show that the sizing of the ore and the uniform small coke have an important bearing on the operation of the furnace. Tests have shown that 3 ft. under the stock line the velocity, temperature and analysis of the gas are uniform across the plane of the furnace. The CO₂ content is exceptionally high. This condition, we feel, is due to the uniform distribution of the sized ore and small coke.

Part of the product is basic iron, which is used in our own plants at Pittsburg, Calif., and Torrance, Calif. The balance is various grades of foundry iron, mostly high-silicon foundry, and these grades require different percentages of manganese and phosphorus, which are controlled in the burden by using high-manganese ore and phosphate rock. Due to making the various grades of iron it is impossible to have a long run on any one particular grade of iron. In the past few months we have had periods during which we have averaged 441 tons of basic iron per day on coke consumption of 1685 lb. of coke per ton of iron. On foundry iron we have had periods averaging 400 tons per day with coke consumption of 1878 lb. of coke per ton of iron.

The average flue dust per ton of iron produced since the beginning of operation is approximately 50 lb., and the maximum wind blown on this furnace to date has been 33,000 cu. ft. per minute.

DISCUSSION

W. R. PHIBBS (written discussion).—Since this paper was presented we have been doing much better work at Provo. We relined our furnace in January, 1928. During May the furnace produced an average of 540 tons of basic iron per day with coke consumption of 1826 lb. per ton of iron, and a maximum individual day of 602 tons. The average tonnage since we have been in blast this year has been 472 tons per day, with an average coke consumption of 1950 lb. per ton of iron. Fifty per cent. of the total tonnage produced has been high-silicon iron averaging 3.00 per cent. silicon. We are blowing an average of 40,000 cu. ft. of wind per minute. The new lines of the furnace give us a cubical capacity of 16,400 cu. ft. As in our previous blast, no scrap has been added to the mixture. The actual yield on the furnace has been 48.6 per cent.

Production of High-alumina Slags in the Blast Furnace*

BY T. L. JOSEPH,† S. P. KINNEY,‡ AND C. E. WOOD,§ MINNEAPOLIS, MINN.

(New York Meeting, February, 1928)

IN connection with its investigations of the blast-furnace process, the Bureau of Mines, in coöperation with the Minnesota School of Mines Experiment Station, developed a 6-ton experimental furnace. Such a furnace was needed to determine the feasibility of producing ferromanganese from Minnesota manganiferous iron ores, a problem of national importance because of the present need for manganese in the steel industry and our small reserves of ferro-grade ores.

Furnace operators are reluctant to use new or untried raw materials or to make decided innovations in practice on account of the financial hazard of experimenting with full-scale equipment. A small furnace which can be operated at a relatively low cost is particularly adapted for testing new raw materials and for determining the feasibility of decided innovations in practice. Laboratory experiments, plus whatever information may be available, are valuable but often do not indicate the net result of changes in an operation involving a large number of interrelated variables.

From time to time the coöperation of the Bureau of Mines is solicited in connection with problems involving departures from normal procedure. Under these circumstances some sort of a practical demonstration is a desirable forerunner to full-scale operations which appear feasible after small-scale tests.

The Aluminum Co. of America was interested in knowing the practicability of smelting a charge of bauxite, iron ore, and limestone, of proportions that would produce slag of the following composition: Al_2O_3 , 47 to 48 per cent.; CaO , 41 to 42 per cent.; SiO_2 , 4 to 5 per cent.; TiO_2 , 2 to 3 per cent.; FeO , 1 percent., and MgO , 1.8 percent. In addition to determining whether it was feasible to operate a blast furnace on slag approaching the composition given above, a quantity of slag was needed for a series of experiments that would show the relative ease and cost of extracting alumina from slag which could be made in the blast furnace, as compared to extracting it from raw bauxite. The value of the slag as a raw material

* Published by permission of the Director, U. S. Bureau of Mines.

† Supervising Engineer and Metallurgist, North Central Experiment Station, U. S. Bureau of Mines.

‡ Metallurgist, U. S. Bureau of Mines.

§ Assistant Chemist, North Central Experiment Station.

for making aluminum, as compared to the value of bauxite for the same purpose, would depend on the relative percentages of alumina available for extraction in the two materials as well as the cost of extraction.

By smelting high-iron bauxites in the blast furnace and subsequently using the high-alumina slag in the production of aluminum the iron which is now wasted would be saved. The effect of alumina on blast-furnace practice has been widely discussed, and its bearing on fuel economy and general efficiency of operation is realized. Because of the possibilities of obtaining information of general technological importance arrangements were made for a three-week test with the experimental furnace. This paper gives a brief résumé of the results of the test, which to the writers knowledge is the first actual demonstration that slags containing from 40 to 50 per cent. alumina can be produced in the blast furnace and that the iron from ferruginous bauxite can be recovered as low-sulfur metal in the same operation. A more complete report¹ will be published later.

INDUSTRIAL FURNACE EXPERIMENTS WITH HIGH-ALUMINA SLAGS

In 1904, the Pennsylvania Steel Co. at its Steelton plant conducted experiments to determine the behavior of high-alumina slags in the blast furnace. McKay,² in describing the experiment, stated:

"By means of Lake ore, chromite, brickbats, and bauxite, a furnace mixture was concocted approximating Mayari ore in chemical composition. The test run lasted 11 days, during which time the furnace averaged 102 tons on a 1 to 1 fuel ratio. This mixture worked with sufficient success as to the character of the slag and the general furnace conditions to warrant a small shipment of ore from the Mayari district. About 1200 tons was transported on muleback from the deposit at El Perio to the sea coast, and shipped to Steelton, where it was tried with more or less success on No. 1 furnace in February, 1906. This test was of six days' duration, the furnace averaging 59.5 tons of iron per day on a fuel ratio of 2.13. The flue dust was excessive, however, and as a result the actual yield of pig iron was but 29 per cent."

In 1914 a much more elaborate series of tests was made over a period of about three months with a furnace of the following dimensions: Hearth, 9 ft., 6 in.; bosh diameter, 15 ft.; stock-line diameter, 11 ft.; and height, 65 ft. The results³ may be briefly summarized as follows:

"During the entire run, the physical condition of the slag has been excellent. After flushes and casts, the runners contained practically no

¹ T. L. Joseph, S. P. Kinney and C. E. Wood: Production of High-alumina Slags in the Blast Furnace. U. S. Bur. of Mines *Tech. Paper* 435.

² Richard V. McKay: Modern American Blast-furnace Practice. *Trans. Amer. Iron and Steel Inst.* (1914) 85-101.

³ R. V. McKay: *Op. cit.*, 98.

cinder, all having drained clean. The slag was invariably hot and exceptionally fluid. With silica plus alumina about 52 per cent., composed of approximately 29 per cent. alumina and 23 per cent. silica, good results were obtained. In fact it developed that variations in alumina from 27 per cent. to 33 per cent. and in silica from 20 per cent. to 25 per cent. had no apparent effect on the operation of the furnace. To me the temperature of the slag appeared far more important than its chemical composition. Our excellent coke gave an intensely hot hearth and no difficulty resulted in handling the slag and obtaining good iron. A slag volume of approximately 1740 lb. per ton of iron was maintained in the various tests. A small amount of mill cinder—6 per cent., running about 29 per cent. SiO_2 —seemed to help the slag conditions by increasing the SiO_2 about 2 per cent. in the slag."

In operating with slags of the composition specified above, McKay found 9 to 10 per cent. MgO very beneficial.

Although the previous information⁴ was of great assistance in determining the advisability of conducting a test on slags containing as much as 50 per cent. of alumina, an actual demonstration was necessary to prove that such slags may be used successfully.

DESCRIPTION OF FURNACE TESTS

The furnace proper and plant layout have been described in previous reports.⁵ About 60 tons of bauxite were used in the test, of the following analyses:

	Al_2O_3	SiO_2	Fe	CaO	MnO	TiO_2	Loss in Ignition
Car 1.....	57.62	2.75	16.77	0.78	0.48	2.64	13.72
Car 2.....	57.06	2.78	16.32			3.08	13.41

The moisture on several samples taken after the bauxite had been unloaded in a frozen condition, stored in a heated building for about three weeks, varied from 9.7 to 13.3 per cent. The structure of the bauxite was favorable, there being only a small proportion of fine material after crushing to 2-in. pieces and smaller.

⁴ J. E. Johnson, Jr.: The Effect of Alumina in Blast Furnace Slags. *Trans.* (1912) 44, 123.

⁵ T. L. Joseph and S. P. Kinney: Minnesota Manganiferous Iron Ores in Relation to the Iron and Steel Industry. *Bull.* 12, Minnesota School of Mines Experiment Station (1927); also T. L. Joseph, E. P. Barrett and C. E. Wood: Minnesota Manganiferous Iron Ores in Relation to the Iron and Steel Industry. *Trans.* (1927) 75, 292.

Limestone

The limestone used in the test was of good quality, containing practically no fine material and no pieces larger than about 2 in. It was not a sized product. Samples from two cars had the following composition:

	CaO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
Car 1.....	53.7	0.64	1.06	0.42	0.50
Car 2.....	53.12	0.60	1.00	0.64	0.48

Coke

By-product coke, known on the domestic market as "nut coke," was used in this test. This size was chosen in order to diminish the oxidizing area in the tuyere zone. With a hearth 36 in. in diameter, past experience has shown that coke of this size is more suitable than larger coke such as is used in industrial furnaces. It is not to be inferred from this that small coke would be better suited for industrial furnaces. The analyses of respective cars follow:

	F. C.	Ash	V. M.	S	Mois-ture	Ash			
						SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO
Car 1.....	90.67	8.38	0.95	0.53	10.1	40.32	21.86	21.86	3.06
Car 2.....	92.30	7.37	0.33	0.55	9.25				
Car 3.....	91.93	7.59	0.48	0.42	10.75	35.24	27.20	28.22	6.12
Car 4.....	91.37	7.81	0.82	0.57	8.20	35.72	29.60	28.83	3.12

The iron ore obtained from the Vermillion range was dense in structure and high in iron as shown by the following analysis:

Fe	SiO ₂	Al ₂ O ₃	CaO	P	Mn	Ig. Loss	Moist.
63.5	4.62	1.16	0.16	0.085	Trace	1.83	4.85

It was essential to use high-grade iron ore to keep the silica in the slag within desired limits.

Cast Turnings

Several small lots of turnings were used in order to increase the production of metal without increasing the silica in the slag. The composition of the various lots follows:

Lot	Per Cent. S	Per Cent. C	Per Cent. P	Per Cent. Si
1	0.08	3.55	0.38	2.26
2	0.08	2.99	0.42	2.26
3	0.09	3.84	0.44	2.26
4	0.07	4.52	0.27	1.87
Av.	0.08	3.73	0.38	2.16

The production of metal was in a sense incidental to the operation inasmuch as the primary object was to convert raw bauxite into a slag containing approximately 50 per cent. Al_2O_3 , 43 per cent. CaO, with the silica as low as possible. The 15 per cent. iron in the bauxite would be recovered and enough iron-bearing materials added to the charge to produce sufficient metal to offset a portion of the operating expenses. The use of borings would permit the production of slag lower in silica and would also allow a larger burden of bauxite, which would increase the slag production. Contrary to normal practice, in which slag may or may not be of sufficient value to pay for its disposal and in which large slag volumes are generally opposed to economical practice, the volume of the slag here would be an important item.

Furnace Lining

Inasmuch as the composition of the slag anticipated in this test differed markedly from normal blast-furnace slags, the lower part of the furnace, including about three-fourths of the bosh, tuyere breast, and crucible, was lined with special material composed of 40 parts of high-grade fireclay and 60 parts of a highly aluminous product (95 per cent. Al_2O_3) which had been fused. After air-drying for several days the temperature was gradually raised until the new section of lining had been thoroughly dried. Examination after the test showed that no appreciable wear had taken place above the zone of fusion, which was well defined at a position about 38 in. above the center line of the tuyeres. From this position downward the thickness of the lining diminished from the original thickness ($4\frac{1}{2}$ in.) until the section above the tuyeres was about $\frac{1}{4}$ to $\frac{1}{2}$ in. thick. On the whole, the condition was similar to that found after tests in which firebrick linings were used. With external cooling only a thin section of lining can be maintained in the lower part of the bosh and tuyere breast. The lining above the fusion zone showed no signs of wear.

First Burden

Inasmuch as slags containing from 40 to 50 per cent. Al_2O_3 had never been produced in the blast furnace, it was necessary to follow information

on melting points and the temperature-viscosity relations of blast-furnace slags. Table 1, compiled from the work of Rankin and Wright,⁶ shows that the melting points of slag containing CaO in excess of Al₂O₃ will, in the range of composition covered, have lower melting points than slags containing alumina in excess of lime. Feild and Royster's viscosity measurements⁷ also show that high-lime slags would be more fluid. Moreover, this work indicates that it is impossible to generalize regarding the relation between viscosity and alumina content, except that the temperature coefficient of viscosity is in general greater for high-alumina content. Blast-furnace slags are not simple mixtures of CaO, Al₂O₃, and SiO₂ but are composed of compounds formed from these oxides. Temperature-viscosity relations do not therefore change directly with gradual changes of a single constituent. After the furnace had been blown in and had come up to temperature, it was decided to adjust the first burden to produce a slag containing more lime than alumina.

TABLE 1.—*Melting Points in Approximate Range of Slags Made in Experimental Furnace*

CaO Higher than Al ₂ O ₃								
CaO.....	60.0	55.0	52.5	52.0	52.0	51.3	50.0	
Al ₂ O ₃	35.0	40.0	42.5	41.2	38.0	41.8	40.0	
SiO ₂	5.0	5.0	5.0	6.8	10.0	6.9	10.0	
Melting point, °C.....	1490	1437	1390	1335	1460	1350	1420	
Al ₂ O ₃ Higher than CaO								
CaO.....	50.0	49.5	49.3	49.0	48.7	48.5	48.3	
Al ₂ O ₃	42.0	43.7	47.7	42.0	39.3	45.0	42.0	
SiO ₂	8.0	6.8	3.0	9.0	12.0	6.5	9.7	
Melting point, °C.....	1375	1335	1482	1390	1430	1361	1380	
CaO.....	47.5	47.0	45.0	45.0	40.0	40.0	39.2	38.0
Al ₂ O ₃	49.5	49.0	47.0	50.0	50.0	45.0	46.0	44.0
SiO ₂	3.0	4.0	8.0	5.0	10.0	15.0	14.8	18.0
Melting point, °C.....	1421	1432	1456	1535	1537	1564	1572	1583
CaO.....	37.8	37.5	37.0	36.7	35.0	35.0	35.0	34.3
Al ₂ O ₃	52.9	53.25	54.0	58.1	50.8	50.0	55.0	52.7
SiO ₂	9.3	9.25	9.0	5.2	14.2	15.0	10.0	13.0
Melting point, °C.....	1512	1505	1509	1549	1552	1550	1590	1570

⁶ G. A. Rankin and F. E. Wright: Ternary System CaO-Al₂O₃-SiO₂. *Amer. Jnl. Sci.* [4] (1915) 39, 1.

⁷ A. L. Feild and P. H. Royster: Temperature-viscosity Relations in the Ternary System CaO-Al₂O₃-SiO₂. U. S. Bur. of Mines *Tech. Paper* 189 (1918).

TEST PERIODS

In order to obtain as much information as possible in the time available, a schedule of tests was followed as closely as conditions permitted. The campaign was divided into four test periods. Operating data, including raw materials and products on a per ton of metal basis, are given in Table 2.

TABLE 2.—*General Operating Data*

Test Period	1	2	3	4	Average
Bauxite, lb. per ton.....	2665	4551	4060	4241	3808
Ore, lb. per ton.....		768 ^a	1353	771	1072 ^a
Limestone, lb. per ton.....	3356	5567	4544	4241	4484
Borings, lb. per ton.....	2145	1720	749	1542	1518
Coke, lb. per ton.....	4572	5690	5013	5551	5127
Carbon, lb. per ton.....	3786	4711	4151	4596	4245
Slag, lb. per ton.....	3574	5490	4634	3480	4785
Metal, tons per day.....	3.12	2.57	3.24	2.78	2.94
<i>Metal Analyses^b</i>					
Carbon, per cent.....	4.55	4.47	4.57	4.90	4.60
Phosphorus, per cent.....	0.37	0.32	0.26	0.36	0.31
Silicon, per cent.....	1.12	0.046	0.079	0.26	0.388
Sulfur, per cent.....	0.008	0.034	0.068	0.023	0.036
<i>Slag Analyses^b</i>					
Lime, per cent.....	44.37	45.65	43.94	39.64	44.11
Alumina, per cent.....	41.36	42.61	45.79	47.24	43.44
Silica, per cent.....	10.22	6.98	6.67	8.46	7.88
Ferrous oxide, per cent.....	0.93	1.09	1.23	1.44	1.17
Titanium oxide, per cent.....	1.57	2.20	2.37	2.12	2.07
Sulfur, per cent.....	1.10	0.52	0.56	0.70	0.72
Blast temperature, °F.....	920	865	870	870	885
Top temperature, °F.....	580	405	425	435	465
Tuyere temperature, °C.....	1785	1720	1640	1625	1705
Slag temperature, °C.....	1600	1550	1550	1570	1568
Metal temperature, °C.....	1485	1440	1430	1425	1450
Blast pressure, inches of Hg.....	4.79	4.74	5.00	5.18	4.85
Blast pressure, lb./sq. in.....	2.35	2.33	2.45	2.54	2.38
Cu. ft. of air per min.....	615	630	645	670	633

^aAverage for only that part of the period during which ore was charged.

^bWeight of flushes and casts considered in obtaining averages for various test periods.

Test Period 1

Perhaps the most interesting phase of the experiment aside from finding that high-alumina slags could be made without difficulty was the low-sulfur metal produced in this test period and also in test 4. One-half

TABLE 3.—Analyses of Individual Casts during Test Period 1

Cast No.	C, Per Cent.	P, Per Cent.	Si, Per Cent.	S, Per Cent.
2	3.01	0.37	6.96	nil
3	2.22	0.40	7.05	nil
4	3.47	0.32	5.85	0.013
5	4.09	0.42	4.13	0.009
6	3.42	0.31	3.47	0.005
7	4.21	0.31	3.61	nil
8	3.93	0.31	3.04	nil
9	4.33	0.34	2.12	nil
10	4.44	0.36	1.87	nil
11	4.57	0.35	1.81	nil
12	4.64	0.37	1.42	nil
13	4.48	0.39	1.13	nil
14	4.71	0.39	1.12	nil
15	4.69	0.36	0.81	0.020
16	4.37	0.37	0.60	nil
17	4.93	0.42	1.12	0.022
18	4.72	0.38	0.63	0.005
19	4.99	0.38	0.51	nil
20	4.40	0.34	0.49	0.003
21	4.75	0.37	0.39	0.031
22	5.01	0.37	0.24	0.015
23	4.95	0.44	0.16	0.010
24	4.85	0.40	0.11	nil
25	4.58	0.38	0.43	0.012
26	4.65	0.35	0.041	0.033

of the first 26 casts contained no sulfur. The turnings charged averaged about 0.08 per cent. sulfur. Changes in the composition of the slag and metal may be followed in Tables 3 and 4.

Test Period 2

Before changing over to a slag which contained alumina in excess of lime it was desirable to determine how iron ore in the burden would affect the operation. During the second test period, which lasted about three and a half days, a burden consisting of 325 lb. bauxite, 394 lb. stone, 50 lb. iron ore, and 100 lb. of turnings was charged the greater portion of the time. This burden is heavier than previous ones which contained no iron ore. Next 100 lb. of turnings was taken off and 50 lb. of ore added. The effect of this change was lower top temperature and slag, metal and tuyere temperatures (see Table 2).

The decrease in hearth temperature is reflected in the composition of the metal; the sulfur increased from an average of 0.008 per cent. for test period No. 1, to 0.034 per cent. for test period No. 2. A further drop in

TABLE 4.—Analyses of Individual Flushes during Test Period 1

Flush No.	SiO ₂ , Per Cent.	FeO, Per Cent.	Al ₂ O ₃ , Per Cent.	CaO, Per Cent.	TiO ₂ , Per Cent.
38*	33.43	0.62	18.48	41.51	0.83
41	33.50	1.45	18.92	39.16	0.50
42	29.84	6.48	22.60	38.37	0.94
42 ^a	29.82	0.76	23.20	41.50	0.37
43	29.72	0.51	24.40	44.15	0.56
44	29.21	0.62	23.97	45.18	0.50
45	30.81	1.44	21.83	42.09	0.48
46	19.73	0.75	34.72	39.32	2.40
47	16.62	0.25	39.70	42.20	1.80
48	11.83	1.00	40.00	47.40	0.76
48 ^a	13.05	1.43	35.32	45.09	0.59
49	11.97	0.01	41.68	46.40	0.44
50	11.92	0.53	39.28	46.82	0.39
51	11.08	0.78	44.70	42.53	0.74
52	11.97	0.56	38.06	46.99	1.09
53	11.02	0.56	41.48	45.48	1.81
53 ^a	7.75	0.36	46.42	44.62	0.34
56	7.69	0.45	44.49	46.86	0.78
56 ^a	9.32	0.40	40.29	49.81	0.80
57	9.09	0.35	41.90	46.50	1.00
58	8.40	0.41	44.84	47.01	0.44
58 ^a	10.10	0.29	41.85	43.15	0.93
59	8.58	0.25	48.01	42.30	0.88
60	9.06	0.20	45.00	43.82	2.05
61	8.69	0.83	44.90	45.09	0.74
61 ^a	11.42	0.59	40.50	45.21	1.78
62	7.96	0.27	43.05	48.55	0.76
63	7.25	0.40	41.39	49.73	0.88
63 ^a	11.69	0.29	41.21	43.15	2.22
64	8.20	0.35	42.00	47.75	0.73
65	8.96	0.54	42.01	46.60	0.68
65 ^a	11.58	2.18	40.46	42.18	2.12
66	7.69	1.38	48.50	38.90	1.86
66 ^a	10.33	1.03	41.76	39.90	2.52
67	9.00	1.34	43.70	42.96	2.45
68	9.74	1.05	42.03	40.48	2.06
68 ^a	10.25	1.30	39.85	43.02	2.00
69	9.35	0.95	40.44	45.39	2.10
70	10.10	1.16	43.46	44.86	1.37
71	6.92	0.44	46.10	46.34	1.61
72	8.72	0.54	46.98	43.60	2.00
73	9.10	1.35	42.09	45.54	1.97
74	8.76	0.76	36.94	52.01	0.98
75	8.22	1.26	38.40	50.59	1.03
76	9.05	1.92	41.17	42.67	2.36
77	8.81	1.86	41.30	43.55	1.97
78	9.76	0.82	41.64	42.93	2.16
79	13.77	0.77	40.01	41.41	2.16
80	7.12	1.86	44.72	43.01	2.32
81	6.59	1.20	43.50	42.99	2.20

^a Slag at cast after flush number indicated.

* MnO content dropped from about 3 per cent. in flush 38 to a small trace in flush 48.

silicon in the metal was apparently caused by the addition of iron ore to the burden. Tables 5 and 6, which give the analyses of slag and metal for the second period, show that the metal contained very small percentages of silicon; the weighted average for the period was 0.046 per cent. With few exceptions, the percentages of ferrous oxide in the slag were not unusually high. Silicon in the metal was oxidized either by the blast or ferrous oxide in the slag. Although there is no means of knowing how much oxidation was caused by the blast, it seems certain that the greater portion of the silicon was oxidized by ferrous oxide. Once oxidized, the basic nature of the slag and the small amount of silica present provided conditions unfavorable to a reentry of silicon into the metal by reduction of silica. Temperatures were high enough to reduce silica, but the small amount in the slag and the presence of iron oxide made this impossible. The average sulfur for the period was 0.034. This increase in sulfur as compared to the first test period was due largely to a decrease in hearth temperature, temperature of slag, metal, and tuyeres. The presence of ferrous oxide would also tend to retard desulfurization.

TABLE 5.—*Analyses of Individual Casts during Test Period 2*

Cast No.	C, Per Cent.	P, Per Cent.	Si, Per Cent.	S, Per Cent.
27	4.78	0.37	0.05	0.026
28	4.88	0.37	0.08	0.017
29	4.77	0.37	0.08	0.024
30	4.35	0.36	0.01	0.066
31	4.25	0.25	0.067	0.060
32	4.27	0.37	0.157	0.024
33	4.19	0.37	0.006	0.007
34	5.03	0.37	0.011	0.004
35	4.59	0.38	0.013	0.016
36	4.32	0.36	0.013	0.022
37	4.95	0.37	0.05	0.016
38	3.25	0.037	0.04	0.13
39	2.43	0.09	0.02	0.051
40	4.50	0.23	0.06	0.06
41	4.63	0.27	0.05	0.04
42	4.54	0.30	0.06	0.02
43	4.36	0.32	0.04	0.04
44	5.09	0.29	0.05	0.04
45	4.53	0.17	0.05	0.04
46	4.65	0.20	0.06	0.054
47	4.19	0.21	0.05	0.051

It is evident from Table 2 that the operation resembled that of a slagging-type producer more closely than that of a blast furnace. However, inasmuch as the primary object of the entire test was to study the

production of high-alumina slags the operation was not typical of either a slagging-type gas producer or a blast furnace. Approximately 2½ tons of coke were used to make about the same quantity of high-alumina slag and 1 ton of pig iron. Most of the metal was obtained from the turnings in the charge.

TABLE 6.—*Analyses of Individual Flushes during Test Period 2*

Flush No.	SiO ₂ , Per Cent.	FeO, Per Cent.	Al ₂ O ₃ , Per Cent.	CaO, Per Cent.	TiO ₂ , Per Cent.
82	6.75	1.35	43.46	39.40	2.15
83	5.90	0.63	41.51	44.95	2.41
84	7.99	0.41	40.80	45.86	2.26
85	7.15	0.19	40.64	46.11	2.20
86	6.81	0.46	42.26	44.08	2.15
86*	11.50	4.26	43.53	37.00	1.93
89	6.53	1.77	46.60	40.92	2.31
92	6.39	0.50	42.22	49.35	2.15
93	6.75	0.28	42.40	49.30	1.91
94	6.51	0.28	40.50	50.90	1.86
95	6.64	0.33	42.18	48.49	2.10
96	6.35	0.35	44.20	48.02	2.00
97	6.44	0.19	40.31	49.39	1.96
98	6.33	1.42	43.01	46.01	2.12
99	6.29	1.44	41.25	48.50	2.21
100	6.87	1.26	43.18	45.62	2.31
101	6.26	1.32	42.10	48.50	2.26
102	6.29	1.13	48.04	43.88	2.31
103	7.23	1.73	44.30	44.75	2.26
113	8.12	1.71	43.00	45.91	2.10
115	7.98	0.90	44.70	45.08	2.25
116	8.41	1.08	49.18	40.40	2.40
117	8.29	0.74	42.80	47.71	2.46
118	7.55	0.77	50.00	41.50	2.36
119	7.19	0.43	43.50	48.12	2.16
120	6.76	0.72	42.03	49.40	2.11
121	7.19	0.84	44.24	43.68	2.46
122	6.40	1.59	41.52	46.28	2.11
123	6.30	1.03	38.24	49.49	2.41
124	6.43	0.79	41.33	48.31	2.36
125	6.33	1.42	41.50	48.00	2.36
126	6.57	1.93	45.50	45.60	2.36
127	6.46	2.70	42.01	47.50	2.31

* Slag at cast after flush number indicated.

Test Period 3

During the first two test periods the average percentage of lime in the slag was greater than the percentage of alumina. However, in the third test period the stone in the burden was decreased. The bauxite in the

change was held constant at 300 lb. and the iron ore at 100 lb., the stone being decreased from 360 to 320 lb. As a result of this decrease in stone the average slag for the period contained about 2 per cent. more alumina than lime. The change to such a slag did not materially change operation of the furnace. There was, however, a large increase of sulfur in the metal, due primarily to a decrease in hearth temperatures. The condition of the tuyeres was not as satisfactory during this period as during the first two test periods. A tuyere log covering the entire test shows a tendency for all tuyeres to skull over. This drop in hearth temperature was due to the increase from 50 lb. of iron ore per round in the previous test period to 100 lb. If more time had been available the changes in composition of slag and the amount of iron ore in the burden would have been made separately and not simultaneously. However, the next test period shows that the change in composition of slag was not responsible for the higher percentages of sulfur in the metal. The analyses of individual casts and flushes are given in Tables 7 and 8.

Test Period 4

One of the objects of this test was to determine whether a slag containing about 50 per cent. Al_2O_3 and 40 per cent. CaO could be produced in a blast furnace. It was fully demonstrated during the last part of

TABLE 7.—*Analyses of Individual Casts during Test Period 3*

Cast No.	C, Per Cent.	P, Per Cent.	Si, Per Cent.	S, Per Cent.
48	4.39	0.23	0.03	0.044
49	4.62	0.21	0.011	0.036
50	4.85	0.24	0.04	0.036
51	4.86	0.20	0.08	0.035
52	4.82	0.26	0.08	0.055
53	4.43	0.24	0.04	0.052
54	4.60	0.26	0.37	0.038
55	4.55	0.26	0.28	0.071
56	4.75	0.25	0.055	0.071
57	4.26	0.25	0.12	0.075
58	4.45	0.24	0.02	0.100
59	4.62	0.23	0.02	0.080
60	4.38	0.25	0.04	0.080
61	4.61	0.25	0.04	0.050
62	4.61	0.27	0.06	0.040
63	3.96	0.23	0.03	0.110
64	4.45	0.29	0.014	0.106
65	4.81	0.32	0.03	0.064
66	4.73	0.33	0.09	0.079

TABLE 8.—*Analyses of Individual Flushes during Test Period 3*

Flush No.	SiO ₂ , Per Cent.	FeO, Per Cent.	Al ₂ O ₃ , Per Cent.	CaO, Per Cent.	TiO ₂ , Per Cent.
128	7.45	2.09	42.32	41.20	2.26
129	6.55	0.88	41.20	49.70	2.25
130	6.28	1.44	43.95	43.54	2.33
131	6.08	0.77	40.88	50.11	2.10
134	5.92	1.13	43.51	48.01	2.21
135	6.12	1.61	44.00	46.68	2.30
136	5.95	0.92	43.88	46.10	2.40
137	5.86	1.97	37.69	51.48	2.16
138	6.25	1.18	44.30	46.74	2.41
139	6.10	1.75	44.01	45.99	2.51
140	6.10	1.57	47.52	44.26	2.51
141	7.22	1.95	44.24	45.50	2.00
142	6.25	2.44	45.18	45.43	2.26
143	6.15	1.74	44.39	45.51	2.31
144	6.21	0.69	48.70	43.39	2.46
146	6.71	0.45	46.59	44.70	2.15
147	6.39	0.51	44.51	45.76	2.40
148	6.61	0.85	47.99	43.00	2.45
149	6.55	1.38	47.88	43.01	2.46
152	6.94	2.72	49.20	40.27	2.27
153	6.41	1.06	47.39	44.40	2.36
154	7.21	0.89	49.61	41.70	2.45
155	7.08	0.81	47.89	43.58	2.40
156	7.45	0.60	46.89	42.34	2.40
157	7.44	0.94	44.82	45.30	2.35
158	7.11	0.93	44.38	45.50	2.45
159	6.70	1.50	51.02	36.88	2.66
160	6.83	1.77	45.28	41.76	2.51
161	7.20	1.27	46.97	43.76	2.51
162	7.45	0.60	46.58	45.17	2.40
164	7.25	0.93	51.76	39.67	2.56
164 ^a	7.04	0.90	49.83	40.25	2.42
166	7.45	0.32	53.91	37.00	2.55

^a Slag at cast after flush number indicated.

the test that this is feasible and the results also showed that under proper conditions low-sulfur metal can be produced. The iron ore was reduced to 50 lb. per round and both the bauxite and stone to 275 lb. Metal produced from this burden was considerably lower in sulfur than that produced from the previous burden, the last five casts varying from 0.001 to 0.007 per cent. The average for the test period, considering the weight of the casts, was 0.023. Tables 9 and 10 show the range of composition of the individual flushes and also give the composition of individual casts. Silica in the slag increased because of increased ash in the coke.

TABLE 9.—*Analyses of Individual Casts during Test Period 4*

Cast No.	C, Per Cent.	P, Per Cent.	Si, Per Cent.	S, Per Cent.
67	4.88	0.34	0.15	0.035
68	4.81	0.35	0.11	0.044
69	4.98	0.38	0.47	0.001
70	4.94	0.36	0.39	0.003
71	4.04	0.40	0.57	0.002
72	4.37	0.39	0.44	0.007
73	4.97	0.34	0.65	0.001

TABLE 10.—*Analyses of Individual Flushes during Test Period 4*

Flush No.	SiO ₂ , Per Cent.	FeO, Per Cent.	Al ₂ O ₃ , Per Cent.	CaO, Per Cent.	TiO ₂ , Per Cent.
167	7.18	1.84	51.61	36.45	2.45
171	7.68	0.80	50.99	38.62	2.40
173	8.67	1.28	46.64	40.24	1.87
175	10.05	3.60	42.00	41.88	1.92
177	9.65	0.80	47.96	38.62	2.15
178	10.02	0.30	51.46	35.47	1.71

GENERAL OPERATION OF FURNACE

In general, operation of the furnace was smooth and free from slips and hanging. The blast temperature was about constant throughout the test. Higher blast heats would have been very desirable but were not possible with the iron pipe stove which was employed in this connection. The top temperatures as shown in Table 2 varied from 405° to 580° F., depending on the burden on the furnace.

Blast pressure indicates a great deal about the operation of a blast furnace. During the entire test the blast pressure was about 2.5 lb. Period skulling of the tuyeres occurred but could probably have been eliminated with higher blast heats. A total of about 70 tons of slag and 30 tons of metal was made during the test. The only difficulties encountered were in connection with tuyere leaks and the iron pipe stove, neither of which was in any way connected with the high-alumina slag.

EFFECT OF SLAG COMPOSITION ON HEARTH TEMPERATURES

The free-running temperature of slag determines its temperature upon reaching the crucible of the furnace. This idea advanced by Johnson⁸ is borne out by temperature measurements made during this test.

⁸ J. E. Johnson, Jr.: Principles, Operation and Products of the Blast Furnace, 39-41. New York, 1918.

Table 11 lists tuyere, slag, and metal temperatures for various practices with commercial furnaces and includes similar results for experimental furnaces. Item 12 confirms the general observations made during the test that the furnace was hotter in the hearth than in previous experiments. The temperature of charcoal-furnace slags approaches the temperature of slag from ferromanganese and spiegel furnaces. Charcoal slags are siliceous, and their composition is in low melting range. Refractory slags pass more slowly through the lower section of the bosh, on account of their high viscosity and, as a result, are preheated to higher temperatures. The ratio of coke to the total charge obviously affects the temperature throughout the furnace, including the hearth. The large quantity of fuel used in the test with high-alumina slags was no doubt partly responsible for attaining higher hearth temperatures than in previous experimental furnace tests. However, the effect of the more refractory slag was shown when the first burden of bauxite reached the hearth. Previous to this time the furnace had been operating on a high burden of siliceous slag containing several per cent. of manganese.

TABLE 11.—*Hearth Temperatures with Various Practices**
Degrees Centigrade

Item	Furnace	Tuyeres	Slag	Metal
1	Pig iron.....	1711	1509	1466
2	Pig iron.....	1708	1526	1472
3	Foundry iron.....	1748	1553	1493
4	Bessemer iron.....	1733	1513	1466
5	Basic iron.....	1669	1522	1468
6	Charcoal.....	1669	1451	1415
7	Manganese alloy.....	1573	1427	1389
8	Spiegeleisen.....	1597	1427	1392
9	Ferromanganese.....	1550	1426	1386
10	Experimental furnace A: pig iron.....	1647	1529	1396
11	Experimental furnace B: manganese.....	1689	1413	1349
12 ^b	Experimental furnace B: high Al ₂ O ₃ , slag.	1705	1568	1450

* Slag and metal temperatures corrected for emissivity, according to G. K. Burgess: Temperature Measurements in Bessemer and Open-hearth Practice. Bureau of Standards *Tech. Paper* 91 (1917), 8; and P. H. Royster, T. L. Joseph and S. P. Kinney: Significance of Hearth Temperatures. *Blast Furnace and Steel Plant* (March, 1924) 154-58.

^b This item not given in previous table.

LOW-SULFUR METAL

One important function of the lower part of the blast furnace is to remove sulfur absorbed by the metal in the upper part of the stack. In normal practice the coke contains about 95 per cent. of the sulfur charged.

A transfer of sulfur from the coke to the sponge iron takes place in the upper portion of the furnace. Metal reaching the region of the tuyeres often contains twice as much sulfur as is permissible in the pig iron. Desulfurization is accomplished by the following reaction:



According to this reaction, desulfurization of the metal is promoted by high lime concentrations and is inhibited by high iron oxide and sulfur concentrations in the slag. The iron oxide in the slag comes from (a) un-reduced ore; (b) oxidation at the tuyeres; (c) formation of FeO by reaction (1); (d) formation of FeO by reduction of SiO₂ with iron; and (e) formation of FeO by reduction of manganese from MnO. The iron-oxide content of the slag is largely controlled by equilibrium conditions for the reaction $\text{FeO} + \text{C} \rightarrow \text{CO} + \text{Fe}$. This reaction is endothermic, and as the temperature is raised the FeO in the slag in equilibrium with carbon in the metal decreases. This is in accord with blast-furnace practice where hot furnaces give low-iron-oxide slags and cold furnaces give high-iron-oxide slags. The exact mechanism of the desulfurizing reaction is not known.

The effect of CaS in retarding reaction 1 depends upon the manner in which the sulfur is removed from the iron. There are at present no data to show whether the greater portion of the sulfur is removed as the globules of iron come in contact with slag in the tuyere region and later pass through the bath of slag, or after the metal has collected at the bottom of the crucible and lies in contact with a layer of slag above it. Calcium sulfide formed at the slag-metal boundary would in the last instance retard the reaction unless it diffused rapidly through the slag. The rate of diffusion of CaS through the slag would be largely controlled by slag viscosity (a function of temperature and composition) and the concentration of CaS at the reacting surface and at other positions in the slag bath. Increased solubility of CaS in the slag would facilitate the absorption of this compound by the slag and would increase its rate of diffusion throughout the slag-bath by virtue of the higher concentrations which would be possible at the slag-metal boundary.

In the case of desulfurization, which takes place as globules of iron pass through the layer of slag, diffusion of CaS would not be as important. The boundary plane between slag and metal would be constantly changing, and the tendency would be to equalize the percentages of CaS in the slag. The area of contact under these conditions favors rapid desulfurization, but the time of contact is short.

A series of preliminary experiments was performed by one of the writers to study elimination of sulfur in the blast furnace. Two types of experiments were conducted. In the first type about 100 gm. of molten metal, containing 0.13 per cent S, was fed through a $\frac{1}{32}$ -in. opening and

allowed to drop through a 10-in. layer (about 450 gm.) of slag held in a graphite container at between 1500° and 1525° C. The time required for the experiment was between 10 and 15 min. In the second type of experiment a sample of the same metal was covered with a layer of slag and the contiguous layers of slag and metal held for 2 hr. at a temperature of 1500° to 1525° C. The weight of metal in the second type of tests was approximately double the weight of slag.

Three slags of the following percentage composition were used:

CaO	MgO	Al ₂ O ₃	SiO ₂	S	MnO	FeO
(1) 47.0		44.6	9.3	0.32		1.2
(2) 42.1	4.7	18.5	32.4	0.01		0.76
(3) 10.44		26.12	31.6	0.57	27.0	3.0

When metal shot were dropped through slag (1) the sulfur was reduced from 0.13 to 0.01 per cent. The same reduction in sulfur took place when molten layers of metal and slag were held in contact with each other at the temperatures given above. Slag (2) reduced the sulfur from 0.13 to 0.029 in the first type of experiment and to 0.022 in the second type. Slag (3) removed smaller amounts of sulfur. The metal from the first type of test contained 0.08 per cent. S and that from the second type, 0.12 per cent.

The foregoing tests indicate that slag of the composition produced in the experimental blast furnace has a strong desulfurizing action. In the opinion of the authors, the desulfurizing action of this slag is due largely to its chemical constitution. Turner⁹ and Schäfer¹⁰ advanced the theory that the spinels alone are capable of reacting with the iron sulfide in the pig iron, the silicates being comparatively inert. The availability of CaO for reaction with FeS depends on the stability of the various compounds which make up the slag.

McCance¹¹ found that when molten aluminum at about 850° C. was added to an equal quantity of FeS at about 1250° C. a rapid reaction took place, forming a slag composed largely of Al₂S₃ and Al₂O₃, the latter resulting from oxidation of the sulfide. If small amounts of aluminum were formed and incorporated into the metal it is possible that some sulfur was eliminated by the formation of Al₂S₃, followed by its separation

⁹ Th. Turner: The Physical and Chemical Properties of Slags. *Jnl. Soc. Chem. Ind.* (1905) 1145.

Th. Turner: Die physikalischen und chemischen Eigenschaften der Schlacken. *Metallurgie* (1906) 164; *Stahl und Eisen* (1906) 26, 172.

¹⁰ I. R. Schäfer: Das Entschwefelungsvermögen der Hochofenschlacke. *Ferrum* (Feb. 8, 1913) 5, 129.

¹¹ Andrew McCance: Non-metallic Inclusions, Their Constitution and Occurrence in Steel: *Jnl. Iron and Steel Inst.* (1918) 97, 254.

from the metal. It does not seem probable that the major part of the sulfur was eliminated in such a manner, but the formation of Al_2S_3 may account for the complete removal of sulfur in some of the casts.

Blast-furnace slags are not mixtures of simple oxides but of more complex compounds. In writing equation 1 it is assumed that thermal dissociation of the lime compounds takes place. The major constituents of the slag produced in this test were $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ and $\text{CaO} \cdot \text{Al}_2\text{O}_3$. Minor constituents were $2\text{CaO} \cdot \text{SiO}_2$; 2CaO , $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$. The desulfurizing power of a slag can not be expressed in terms of its percentages of CaO because the activity of the lime toward FeS will depend upon the thermal dissociation of the compounds making up the slag. Complete information is not available to show the degree of thermal dissociation of the various compounds which exist in blast-furnace slags. Practice shows, however, that basic slags containing large amounts of the compounds listed above desulfurize more readily than acid slags, in which a part of lime is present as $\text{CaO} \cdot \text{SiO}_2$; $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$; $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ and $3\text{CaO} \cdot 2\text{SiO}_2$.

McCaffery and Oesterle¹² have shown that alumina increases the solubility of slag for calcium sulfide. However, the increase in solubility is small. At 1500°C . mixtures of CaO, Al_2O_3 and SiO_2 in the range of blast-furnace slag were found to dissolve about 10 per cent. sulfur. Blast-furnace slag usually contains about 2 per cent. sulfur, so it appears that so far as solubility is concerned normal percentages of sulfur are about 20 per cent. of the amount required for saturation. At the slag-metal surface concentrations higher than 2 per cent. are probably attained. Exact information on this point, however, is entirely lacking. Although the work of McCaffery and Oesterle indicates that the high-alumina slag produced in the experimental furnace would dissolve more CaS than ordinary slags its unusual desulfurizing power was, in the opinion of the writers, due primarily to the fact that lime held as aluminaates is more active toward FeS than lime in the compounds existing in the range of normal slag composition. The large volume of slag per ton of metal aided the production of low-sulfur metal. However, test periods 1 and 4, with lower slag volumes, lower burdens, and higher slag temperatures than periods 2 and 3 (Table 2), show the effectiveness of temperature.

The writers believe that experimental data are needed to establish the relative importance of the factors affecting the velocity of the reactions involved in desulfurization. Continuation of the preliminary experiments on a more comprehensive scale is therefore being planned.

In the present test the high-alumina slag lost its strong desulfurizing power as the temperature fell off. The effect of temperature was proba-

¹² R. S. McCaffery and J. F. Oesterle: Desulfurizing Power of Blast-furnace Slags: *Trans. (1923)* 69, 606.

bly twofold; it produced greater thermal dissociation of the compounds making up the slag and also increased the reaction rate.

OXIDATION OF SILICON FROM THE BORINGS CHARGED

Reference has been made to the oxidation of silicon. The tuyere zone of the experimental furnace is more oxidizing than the tuyere zone of a larger furnace, because the hearth of the experimental furnace is smaller. Although the smaller coke (nut size) reduced the oxidizing area in the combustion zones the large strongly reducing area present in the central portion of industrial furnaces did not exist in the experimental furnace. In the experimental furnace the O_2 disappeared at about 13 in. from the nose of the tuyere and the CO_2 disappeared at about 18 in. In an industrial furnace with a 20-ft. hearth the combustion zones extend about 30 to 40 in. beyond the tuyeres, leaving a large strongly reducing area in the central portion of the furnace. Although it is impossible to determine the silicon content which might be expected in metal produced in a full-size industrial furnace it should be higher than is the metal made in the experimental furnace.

SUMMARY AND CONCLUSIONS

In the absence of any experimental evidence that a blast furnace could be operated on a burden of iron ore, bauxite, limestone, and scrap, melting-point determinations were an invaluable guide in predicting the behavior of high-alumina slags. Melting-point determinations indicate that it would be feasible to operate a furnace on slags containing 47 to 48 per cent. Al_2O_3 , 41 to 42 per cent. CaO , 4 to 5 per cent. SiO_2 , and small percentages of TiO_2 , MgO and S. In general, slags containing CaO and Al_2O_3 in about equal amounts will have the lowest melting points when the percentage of CaO exceeds the percentage of Al_2O_3 .

Viscosity determinations in the ternary system $CaO-Al_2O_3-SiO_2$ show that the ternary eutectic, composed of 49.5 per cent. CaO , 43.7 per cent. Al_2O_3 , and 6.8 per cent. SiO_2 , has relatively low viscosity and that only a small change in viscosity takes place with changes in temperature above the melting point.

Although there was evidence that a blast furnace could be operated on slags containing about equal percentages of lime and alumina with 6 to 10 per cent. silica, some sort of a practical demonstration was needed to obtain positive information. It was desirable furthermore to obtain a substantial quantity of slag to determine the relative ease of extracting alumina from high-alumina slag as compared with extracting alumina from crude bauxite. Operating data from the experimental furnace were also needed to determine the economic possibilities of treating high-iron bauxite in the blast furnace to produce a calcium aluminate slag for the manufacture of aluminum.

During a two-week test, experimental furnace slags were produced covering a range of composition, as follows: 6 to 33 per cent. SiO_2 , 35 to 52 per cent. CaO , 18 to 53 per cent. Al_2O_3 , about 2 per cent. TiO_2 , about 1 per cent. FeO , and 0.5 per cent. S. There was no difficulty in operating the furnace on slag varying over this wide range of composition. The temperature-viscosity relations of slag do not change directly with gradual changes of a single constituent. Although alumina increases viscosity in some ranges of composition in others it decreases viscosity. Metal low in sulfur was produced due to the temperature of the slag, to its large volume, and primarily to the availability of the lime for reacting with iron sulfide.

High-alumina slags lose their strong desulfurizing power at lower temperatures. Preliminary laboratory tests show that calcium aluminates desulfurize metal rapidly at 1500° to 1525° C. Although there is experimental evidence to show that CaS is more soluble in slags containing higher percentages of alumina the marked capacity of such slags to desulfurize metal is attributed largely to the basicity of the slag or the amount of lime which is available to act as a driving force in the formation of CaS.

Silica was oxidized from the borings charged because the blast had an oxidizing effect in the combustion zone and, moreover, unreduced iron oxides reached the hearth. The marked oxidation of silicon from scrap charged in the experimental furnace would be much less pronounced in full-size furnaces.

ACKNOWLEDGMENTS

The writers wish to acknowledge the active assistance of Francis C. Frary, director of research of the Aluminum Co. of America. The practical operation of the 6-ton furnace used in the test described in this report was under the direction of Charles Ash and Eli Webb, two competent furnace men. Chemical analyses of raw materials and products were made by F. W. Holbrook, of the Bureau of Mines, and Mr. Svenson of the Aluminum Co. of America.

DISCUSSION

J. M. GAINES, JR., Pittsburgh, Pa.—The question of making low-sulfur metal is very interesting, but if you analyze the figures given on page 72 in the general operating data of the four test periods, you will find that actually the small experimental furnace with its high-alumina slags did not do any better than an ordinary blast furnace, except on the first run. The ratio of the percentage of sulfur in the slag to that in the metal, which would act as an indicator of the desulfurizing power of that furnace, during the first period is 133, and there is a very high tuyere temperature of 1785° C. On the next one the ratio drops to 15, on the third it is 8.2, on the fourth it is 30, with a general average of 48. I have figures on a 300-ton furnace at which, during a period when it was actually jammed up and hardly making iron at

all, gave a ratio of 18, which is higher than two of the periods of the experimental furnace, and under normal operation an average of 87. This furnace was operating with a maximum tuyere temperature of 1620°, which is lower than any of the temperatures given in the experimental heats. It is a question, therefore, whether the credit for desulfurizing in the experimental furnace should not be given to the large volume of slag present and the high temperatures carried rather than to the high alumina content of the slags.

T. L. JOSEPH (written discussion).—The idea that the experimental furnace operating on high-alumina slags desulfurized throughout the test more effectively than an industrial furnace operating on normal slags is neither expressed nor implied by the authors. Unusually low-sulfur metal as well as high-sulfur metal was produced during the test. Anyone familiar with blast-furnace practice will be impressed with the fact that conditions during the first test period were unusually favorable to the production of low-sulfur metal. Over a period of several days one-half the casts contained no sulfur. The fourth test period was short but the last five casts of this period contained sulfur varying from 0.001 to 0.007 per cent. The authors have expressed in the paper their opinion as to why it was possible to produce metal so unusually low in sulfur.

As explained on page 78, a decrease in the burden at the beginning of test period 4 resulted in a decrease in the sulfur from 0.079 per cent. for the last cast of test period 3, to about 0.003 per cent. for the average of the last five casts in test period 4. This large change in sulfur content indicates that the desulfurizing power of high-alumina slags depends a great deal upon temperature. As pointed out on page 83, "Test periods 1 and 4, with lower slag volumes and higher slag temperatures than periods 2 and 3, show the effectiveness of temperature." The extremely low sulfur was not due solely to any one factor, but as explained on page 83 and again on page 85, it was due to the combined effects of slag temperature, slag volume and the basic nature of the slag or the high available lime content for reacting with iron sulfide.

In order to learn something of the effect of composition alone, laboratory tests reported on page 82 were made. Under similar conditions of slag volume and slag and metal temperatures, the high-alumina slag reduced the sulfur from 0.13 per cent. to 0.01 per cent. in both the dropping and bath-type tests while slag of about normal composition reduced the sulfur from 0.13 per cent. to 0.029 and 0.022 per cent., respectively, for the dropping and bath-type tests. The same completeness of desulfurization was effected in the laboratory tests with high-alumina slag as was produced in the experimental furnace during test periods 1 and 4. While the production of metal containing only traces of sulfur was undoubtedly due to several factors all favoring desulfurization, the authors believe that the completeness of sulfur removal from the metal was due primarily to the basic nature of the slag. In their opinion, a combination of high slag volume, high temperatures and normal slag composition would not have resulted in such complete removal of sulfur.

Utilization Problems of Metallurgical Limestone and Dolomite*

BY OLIVER BOWLES†, NEW BRUNSWICK, N. J.

(New York Meeting, February, 1928)

WHILE vast quantities of limestone and dolomite are used in metallurgy, the estimated production in 1926 being 23,860,000 tons, there are many problems connected with their use which have not received adequate study. The literature of metallurgy is notably lacking in comprehensive discussions of fluxing or furnace stone. Approximately 900 lb. of limestone is used for every long ton of pig iron produced in the blast furnace, but this important constituent of the charge receives little attention compared with the intensive study that has been applied to ores and fuels, the other important constituents of the charge.

In an effort to elucidate some of the doubtful points, the writer has made a wide review of metallurgical literature, and has had the disappointing experience of finding not more than a paragraph or two on metallurgical stone for each two or three thousand pages of literature reviewed. Furthermore, the limited information supplied is in some instances contradictory and even absurd. For example, a correspondent in a reputable metallurgical magazine classifies magnesia and silica together as impurities in flux "that must be melted and run off as slag."

From the furnace operator's viewpoint it is desirable that as complete knowledge as possible be obtained concerning the effects of chemical composition and physical character of the stone on its action in the furnace and on the quality of the metal produced. A better knowledge of these features is advantageous also to the quarry operator in that it enables him to work more intelligently in producing stone that will best satisfy the metallurgists' requirements.

The following pages comprise a brief compilation of data now available. Much of the information is well established and probably acceptable to most metallurgists. On some points there is room for debate, and the chief purpose in presenting a paper at this time is to arouse discussion which will throw more light on controversial points and thus assist the author in preparing a more comprehensive and accurate discussion of metallurgical limestone problems.

* Published by permission of the Director of the U. S. Bureau of Mines.

† Supervising Engineer, Non-metallic Minerals Experiment Station, U. S. Bureau of Mines (in coöperation with Rutgers University).

BLAST-FURNACE FLUX

The chief impurities in most iron ores are silica and alumina, and the addition of a basic flux is necessary to form a slag. If iron ore were reduced without flux, the siliceous and argillaceous gangue would unite with the iron oxides to form double silicates of iron and alumina, which would involve a heavy loss of iron. With the addition of limestone, the silica and alumina have a stronger affinity for the lime and magnesia than they have for the iron, and in consequence double silicates of lime and alumina or magnesia and alumina are formed—compounds which contain very little iron. Just as an acid and a base react to form a salt, so the siliceous impurities of the ore react with the basic flux to form a slag which corresponds to the salt of wet chemistry. Lime is infusible at the temperature of a blast furnace, but when it combines with the silica and alumina of the furnace charge it forms a liquid slag which floats on the molten iron.

At the fusion zone, approximately 15 per cent. of the original iron exists as FeO, and this must be reduced in the lower part of the furnace. With insufficient flux a black slag containing iron is likely to be made during the reduction process. It is true, however, that a normal supply of lime will not in itself prevent loss of iron in the slag; other conditions must also be correct.

Coke is used as blast-furnace fuel, and when it burns varying amounts of ash are formed. The ash is composed largely of silica and alumina, which, like the similar impurities in the ore, must be removed. Therefore the formation of a slag with the ash is a secondary function of the limestone flux. The slag should pick up the coke ash in the combustion zone, for it is desirable to remove the ash which forms on the coke lumps in order that the coke surface shall be clean. Inasmuch as the combustion zone is the seat of life in a furnace, it is not only necessary to remove the ash but also to produce a slag which will pass freely through this part of the furnace. An improper slag adheres to the coke and is chilled by the blast. This results in a sluggish tuyere, and tuyere action must be carefully controlled by the furnace operator. The slag should have a melting point below the average tuyere temperature, and should be fluid enough to pour out readily through the cinder notch.

Another purpose of the flux is to remove sulfur from the metal. Most of the sulfur enters the furnace in the coke, but there is a transfer of sulfur from the coke to the sponge iron. Even when it has reached the bosh of the blast furnace, metal often contains twice as much sulfur as is permissible in the pig iron. Proper additions of flux with necessary temperature adjustments reduce the sulfur to specified limits.

In some localities, iron ores are associated with sufficient lime carbonate to be self-fluxing. Ores are said to be self-fluxing when the sum of

the calcium and magnesium oxides is approximately equal to the sum of the silica and alumina. Such ores occur in the iron district of Birmingham, Alabama. They smelt very readily, as the constituents are intimately mixed.

Action of Flux in the Furnace

When subjected to the heat of the furnace, the limestone in the charge is first converted to CaO (lime) and CO₂ (carbon dioxide). The lime reacts with the impurities to form slag. Precalcined lime is said to combine more readily with the impurities than the lime formed by calcination in the furnace, but the extra cost of precalcination probably more than offsets this advantage. Calcination of CaCO₃ in the furnace is more economical than precalcination because usually there is sufficient available heat in the upper part of the furnace, and the heat used for calcination would otherwise be lost as sensible heat in the waste gases.

Alumina may be regarded either as an acid or a base, for it will combine with silica to form aluminum silicate, thus performing the office of a base, or it will unite with lime to form calcium aluminate, acting in this case in the capacity of an acid. In ordinary blast-furnace practice, silica and alumina (SiO₂ and Al₂O₃) are regarded as acids and the lime and magnesia (CaO and MgO) as bases. Feild and Royster¹ found that in general the effect of increasing the Al₂O₃ content of slags is to increase viscosity and melting temperatures, though under some conditions this may not be true. In general, therefore, the presence of excessive alumina in either flux or ore not only requires a correspondingly large amount of calcium or magnesium to neutralize it but also demands additional heat units to give the resulting slag the desired fluidity. On this account, the clay content of fluxing stone should be kept at a minimum.

Definite data on lime-alumina-silica compounds in the liquid phase of slags are not now available. It is generally assumed, however, that for efficient sulfur removal an excess of limestone should be added above that required to satisfy the demands of the silica and alumina present.

McCaffery and Oesterle² found that the effect of alumina was to increase the solubility of the slag for calcium sulfide, but to decrease its solubility for manganese sulfide; also, that temperature is a much more important factor than chemical composition in its effect on the sulfur solubility of the slag. Therefore, for the most effective reaction, a high temperature should be maintained, for at high temperatures the slag will more completely desulfurize iron than at low temperatures. This is probably due to increased rates of interchange between slag and metal

¹ A. L. Feild and P. H. Royster: Slag Viscosity Tables for Blast-furnace Work. U. S. Bur. of Mines Tech. Paper 187 (1918) 20. Also Trans. (1918) 58, 654.

² R. S. McCaffery and J. F. Oesterle: Desulfurizing Power of Iron Blast-furnace Slags. Trans. (1923) 69, 624.

at the higher temperature, more complete deoxidation of the slag at the higher temperature, and to the fact that a more basic slag can be carried. Sulfur and other impurities are best removed where the slag has a high fluidity.

Effects of Impurities on Fluxing Stone

The majority of blast furnaces employ about 900 lb. of flux for each long ton of pig iron produced. The amount of flux required varies with the amount and nature of the impurities in the ore and in the stone itself. The foreign elements in fluxing stone are usually the same as those in the ore for the removal of which the flux is added; namely, silica and alumina. It should be emphasized that impurities in the limestone are doubly detrimental; in the first place, their presence reduces the percentage of lime and magnesia in the stone, and in the second, they require a certain share of the lime and magnesia to flux them off, as the flux must neutralize its own impurities as well as those of the ore.

"Available carbonate" is a term applied to the percentage of calcium and magnesium carbonates available for fluxing the ore after a sufficient percentage has been deducted to neutralize the impurities in the stone itself. In the average blast-furnace slag the ratio of $\text{SiO}_2 + \text{Al}_2\text{O}_3$ to $\text{CaO} + \text{MgO}$ is about 1 to 1. Thus for every pound of silica and alumina present in a high-calcium flux, 1 lb. of lime is required to flux it. A pound of lime (CaO) is derived from 1.785 lb. of limestone (CaCO_3); hence if there are 4 lb. of $\text{SiO}_2 + \text{Al}_2\text{O}_3$ in each 100 lb. of the stone, not only does the stone lose this 4 lb. of impurity, but also 4 by 1.785 lb. of pure limestone which is required to flux the impurity—that is, a total of 11.14 lb., and the "available" carbonate in each 100 lb. of stone is only 88.86 lb. This may be expressed in a general formula as follows: If A = the percentage of $\text{SiO}_2 + \text{Al}_2\text{O}_3$ in the stone, the available carbonate is $100 - A - 1.785A$, or $100 - 2.785A$. Where a dolomite is employed it requires about 1.914 lb. of stone to give 1 lb. of the combined oxides of calcium and magnesium. Hence for a dolomite flux the general formula for determination of available carbonate becomes $100 - 2.914A$. Most fluxing stone used in the United States runs under 10 per cent. magnesium carbonate, and hence the conversion factor may be taken as 1.8 and the general formula as $100 - 2.8A$.

Another disadvantage in using impure stone is the formation of additional slag, which increases the fuel consumption. Extra slag requires extra coke but there is a difference of opinion as to how much extra coke is needed. As other conditions may affect the amount of coke required for each additional pound of slag formed, it is difficult to arrive at an actual figure for the additional fuel cost when an impure stone is used. If A = the sum of per cents. of silica and alumina in the stone, the slag formed from these impurities will be approximately $2A$. If it is

assumed that x lb. of coke are required for each pound of slag, the extra coke required to flux the impurities in the stone will be $2Ax$ lb. for each 100 lb. of stone. Hence, any blast-furnace operator who has determined a figure for the amount of coke required for each additional pound of slag formed can estimate closely the additional fuel expense caused by the use of impure stone. Assuming a value of y cents per ton for metallurgical coke, the extra cost of fuel on account of impurities in the stone will be $\frac{2Axy}{2000}$ or $\frac{Axy}{1000}$ c. for each 100 lb. of stone. For each ton of stone this will be $\frac{20Axy}{1000}$ or $\frac{Axy}{50}$ cents.

A third source of loss due to impurities in the stone is reduced furnace output. Furnace output for a given ore is, in general, inversely proportional to coke consumption per unit of slag, and as the extra slag requires extra coke, furnace production may be cut down to some extent, though the exact amount is governed somewhat by the amount of wind blown. T. L. Joseph³ has found that for 50 furnaces investigated the number of pounds of coke burned per square foot of hearth area per minute varied from 2.5 to 5.5. If the same wind is blown and the fuel consumption goes up, the iron tonnage will decrease. There are, however, no definite standards for rates of blowing. If a furnace were blown a little faster to compensate for an increase in fuel consumption arising from the use of low-grade stone, the furnace output might not suffer any reduction. If unusually impure stone were used, the output might be reduced.

If V = the price in cents of pure stone per ton, and V' = the price of impure stone, disregarding the possible reduction in furnace output and combining the two chief sources of loss—namely, the reduction in available carbonate and the extra fuel required,

$$V' = V(1 - 0.028A) - \frac{Axy}{50}$$

By substituting any given values for percentages of impurities, pounds of coke per pound of slag, and value of coke per ton, a fairly definite figure may be obtained for the value of an impure stone as compared with a pure stone. If the value of an impure stone as thus calculated is lower than the actual cost at which such stone may be delivered at the furnace, it would be more profitable to use the higher priced pure stone. Macoun⁴ states that each decrease of 1 per cent. SiO_2 between 5 per cent. and 1 per cent. amounts to a reduction in cost of approximately 10 c. per ton of limestone, because it saves coke, increases production, and lowers operating cost.

³ Personal communication.

⁴ A. E. Macoun: Recent Blast Furnace Advancement. *Blast Furnace & Steel Plant* (1915) 49, 671.

Other impurities in the stone are sulfur and phosphorus, but usually they are present in amounts so small as to be negligible. A sulfur content of less than 0.1 per cent. does no harm, and it is unusual to find more than this amount in commercial limestone. Hall⁵ states that for 110 analyses of Pennsylvania limestones given in State College reports of 1899 and 1900, the average sulfur content was only 0.08 per cent., while in 163 analyses sulfur was ignored because there was so small an amount. Phosphorus is usually deleterious only where the flux is used in the manufacture of Bessemer iron. For this purpose the phosphorus content should be as low as possible, and should not exceed 0.01 per cent. For other grades of iron the phosphorus content may reach 0.1 per cent. without harmful results, and a content as high as this is exceedingly rare.

Slagging Effect of Magnesia

The effect of magnesia in fluxing stone is an unsettled question. Some blast-furnace men are opposed to its use while others use it successfully. Dolomite is widely used as a blast-furnace flux in England. If it is assumed that all the magnesia unites with silica to form $MgSiO_3$, and all the lime unites with silica to form $CaSiO_3$, it would appear that magnesia is the better fluxing agent, for 1 lb. of MgO will convert 1.51 lb. of SiO_2 into $MgSiO_3$ and 1 lb. of CaO will convert 1.08 lb. of SiO_2 into $CaSiO_3$. It is probably on this basis that Forsythe⁶ makes the statement: "MgO has a fluxing power 1.4 times that of CaO." This is not a safe assumption, however, for other compounds are also formed, such as dicalcium and tricalcium silicates, also calcium and magnesium aluminates. Much is still to be learned concerning the proportion of such compounds formed under varying conditions, and the effect on slag viscosity of the various possible compounds.

As the result of some recent valuable research, McCaffery and Oesterle⁷ claim that MgO cannot be added in an amount corresponding to the chemical equivalent of CaO , for with the addition of MgO some magnesian minerals, such as pyroxene, forsterite or akermanite are formed, and the physical characters of these minerals may differ greatly from those of the calcium minerals such as anorthite or calcium bisilicate, which might otherwise be present. A slag consists almost entirely of compounds of the primary components (CaO , MgO , Al_2O_3 , SiO_2) and it is really the variation of the properties of these compounds that changes the properties of the slag. The authors found that 18 compounds of the four primary components may be present. In discussing McCaffery and

⁵ R. D. Hall: Discussion. *Trans.* (1920) 63, 927.

⁶ R. Forsythe: Blast Furnace and the Manufacture of Pig Iron (1922) 160. U. P. C. Book Co.

⁷ R. S. McCaffery and J. F. Oesterle: The Constitution of Iron Blast Furnace Slags. *Year Book*, Amer. Iron Steel Inst. (1924) 285.

Oesterle's paper, B. E. Pheneger said that magnesia should be added to give increased fluidity; also, that 19 operators in Lake ores agreed that their practice is adversely affected if the magnesia content of the slag exceeds 6 per cent. In what way it is adversely affected is not clear, but one would infer from the context that improper sulfur removal is the chief objection. Reference is made to the fact that at times high-magnesia slags become less fusible and exhibit increased viscosity.

In further discussion of the paper, G. M. Hohl does not agree that 3 to 5 per cent. MgO in the slag should be the limit for good practice, for at Bethlehem the slags average 17 to 19 per cent. MgO and the sulfur content and the coke consumption are no higher than at plants using low-magnesia stone. Carnegie⁸ says that for blast-furnace flux "the presence of a large quantity of carbonate of magnesia in the limestone increases the quantity required per ton of iron produced, and in consequence the cost is greater." Such a statement conflicts with the claim that MgO has a greater fluxing power than CaO. From the information now available, it would appear that lime and magnesia are about equally effective for the removal of silica and alumina.

Magnesia as a Sulfur Remover

Magnesia is generally regarded as less efficient than lime as a sulfur remover, but here also there is a difference of opinion. Johnson⁹ refers to Sir Lothian Bell's opinion that magnesia is inert as a sulfur remover, but makes the definite statement that in his opinion magnesia is just about as efficient as lime. It is probable that very few metallurgists will agree with this statement.

One author, in referring to the preference for dolomite at Alabama furnaces, went so far as to conclude that the magnesia must be a better desulfurizing agent than lime, but the real reason why dolomite is preferred at the Alabama furnaces in question is not because of any preference for magnesia but because the dolomite has a lower silica content (1.25 per cent. as against 3.5 per cent. in the high-calcium stone), and also because of a greater uniformity in the composition of the dolomite.

Effect of Magnesia on Slag Viscosity

Much difference of opinion seems to exist as to the effect of magnesia on the viscosity of slags. In a number of tests covering the smelting of various metals, the statement is made that magnesia tends to make the slag ropy and viscous; in fact, it is mentioned so frequently by practical operators that it seems to be established as a fact in many instances. This conclusion, however, would seem to conflict with theory. It is a

⁸ David Carnegie: Liquid Steel, 30. New York, 1918. Longmans, Green & Co.

⁹ J. E. Johnson, Jr.: Principles, Operation and Products of the Blast Furnace, 206. New York, 1918.

well-established principle that a silicate with more than one base fuses at a temperature lower than a one-base silicate. Johnson¹⁰ states that "the addition of a certain amount of magnesia has a marked effect in lowering the fusion temperature of the slag." He refers to the experiments of the Swedish investigator, Akerman, who found that the most fusible slag consisted of two parts lime to one part magnesia. Morgan¹¹ says "the presence of much magnesia in the stone tends to make the resulting slag less refractory." Maccoun¹² claims that for spiegel and ferromanganese a mixture of one-half calcite and one-half dolomite is preferable to a high-calcium flux, as it "gives a more fluid cinder, permits a more basic slag, and thus keeps manganese loss low."

On the other hand, Hofman¹³ regards magnesia as undesirable in a lead furnace, as it makes a pasty slag. Gowland¹⁴ states that magnesia is objectionable, giving pasty slags in both lead and copper smelting.

Herty¹⁵ believes that high-magnesia (open-hearth) slags are almost always viscous and require an undue amount of working with fluorspar or some other "thinning" agent.

Feild and Royster¹⁶ found that the temperature viscosity relations of an iron blast-furnace slag were practically unaffected by the presence of magnesia up to 14 per cent., but no statement is made regarding higher percentages of magnesia.

The seeming conflict is possibly explained by the fact that slags consist of quite a number of components combined in complex ways in consequence of which it is very difficult to determine just what result would ensue from increasing a single component. This seems to be the conclusion reached by Feild and Royster, as they say: "The most important conclusion to be drawn from the results of the investigation is that a slag, even when melted and completely converted into a liquid, is composed of relatively complex compounds of lime, alumina and silica, and not of a simple mixture or solution of the constituent oxides CaO, Al₂O₃, and SiO₂. The temperature-viscosity relation of the slag is not therefore . . . changed continuously and in the same general direction by the gradual addition of a single constituent." It seems possible, therefore, that under some conditions an increase in the magnesia content may

¹⁰ *Op. cit.*, 245.

¹¹ J. J. Morgan: *Blast Furnace Practice*, 5. 1910. J. B. Lippincott Co.

¹² A. E. Maccoun: *Recent Blast Furnace Advancement. Blast Furnace & Steel Plant* (1915) 49, 671.

¹³ H. O. Hofman: *The Metallurgy of Lead*. 1918. McGraw-Hill Book Co., Inc.

¹⁴ William Gowland: *The Metallurgy of Non-ferrous Metals*, 49. 1921. C. Griffin & Co., Ltd., London.

¹⁵ C. H. Herty, Jr.: *Burnt Lime and Raw Limestone in the Basic Open-hearth Process*. *Ind. & Eng. Chem.* (1927) 19, 592.

¹⁶ A. L. Feild and P. H. Royster: *Slag Viscosity Tables for Blast Furnace Work*. U. S. Bur. of Mines *Tech. Paper* 187 (1918) 5. Also *Trans.* (1918) 58, 650.

result in a more viscous slag, and under other conditions in a more liquid slag.

It is possible that the amount of alumina present may greatly affect the viscosity. Forsythe¹⁷ makes a significant statement in this connection, as follows, "With tolerably pure silicate slags having less than 5 per cent. Al_2O_3 , the proportion of MgO need be of little concern, since successful slags have been run with CaO as low as 12 per cent. If Al_2O_3 exceeds 10 per cent., however, MgO in excess of 20 per cent. causes too much viscosity in the cinder whereby it becomes sticky and does not work freely."

Confusion may result also from the use of the terms "melting point" and "free-running temperature," for these may differ widely. Some slags have a short range of viscosity while in others it is long. The former may be compared with ice, the latter with tar. The formation temperature of a slag bears no definite relation to its flowing temperature. From the standpoint of slag viscosity, the free-running temperature is of more importance than the melting point.

As a rule, high-calcium fluxes are preferred, but the difference in action between the high calcium and the dolomitic fluxes is so small that usually the choice is governed by other factors, such as availability, cost, or percentage of impurities.

Effect of Magnesia on Slag Utilization

Where crushed or granulated slag is used for concrete aggregate or road building, as a substitute for crushed stone, the magnesia content is not generally regarded as important. However, in a recent communication from a company producing very large quantities of fluxing stone, the statement is made that some blast-furnace operators are requesting stone with 7 to 10 per cent. magnesia because the resulting slag is more desirable for roadmaking. The advantage is probably due to the decreased slaking effect in the high-magnesia slags.

Slag is now used extensively for the manufacture of Portland cement. For this, the flux must provide a slag having a magnesia content within the fairly narrow limits demanded by cement specifications.

Factors Governing Use of Impure Fluxing Stone

The cost of stone delivered at the furnace commonly has a very direct bearing on the quality of stone used. This is due to the fact that an inferior stone may be used if the price is low enough. The question of quality is so intimately related to cost that the problem of purity of blast-furnace flux becomes quite complex. In order to clarify this point, it is necessary to make a distinction between impurities. In general, they

¹⁷ *Op. cit.*, 160.

fall in two classes. Some, such as sulfur and phosphorus, are detrimental to the quality of the iron produced, hence the use of stone containing excessive quantities of these impurities could not be justified, no matter how low the price.

The other more common and abundant impurities are silica and alumina, which are not regarded as detrimental to the iron, their chief disadvantages, as pointed out, being the requirement of additional limestone and coke to convert them into slag. Suppose that a relatively pure stone and an impure stone are both available, and that the impurities are of the silica-alumina type, which has no detrimental effect on the iron. If the price of the impure stone is low enough to overcome the disadvantages, the impure stone may be used in preference to the pure stone. Thus at Bethlehem, Pa., a stone quarried near the furnaces, running as high as 5 per cent. silica, is used extensively in preference to the low-silica stone from McAfee, N. J., because the transportation charge from McAfee is greater than the total cost of quarrying the impure stone. The quality of the ore also influences the degree of impurity permissible in the flux. Thus it would not be wise to use a flux high in silica with a high-silica ore.

It is evident from the above that no definite rules can be laid down regarding the purity of a stone that may be used for flux. A stone that might be condemned in one locality might be quite acceptable in another where the conditions were different. The direct bearing of cost on use indicates how important it is to be able to calculate even approximately the relation between percentage of impurities and price. Usually the use of an impure stone can be justified only where it has the advantage of close proximity to the furnace, thus eliminating the usually heavy item of transportation expense.

Size of Stone for Blast-furnace Flux

Fluxing stone is used in a great variety of sizes. At some furnaces the crusher run is used directly without screening. Usually the fines below $\frac{1}{2}$ in. are taken out, partly because they tend to retard the draft and partly because they usually contain more impurity than the lump stone, as sand and clay segregate in the fines. In modern quarry practice, and particularly in underground mining, there is less impurity mixed with the stone than during former years under cruder practice; therefore, on the basis of purity, fine materials may not be detrimental. A common range in size is $-4\frac{1}{2}$ in. $+1\frac{1}{2}$ in., though larger sizes are often used.

It is probable that the finer sizes are less detrimental than the demands would seem to indicate. In the course of visiting quarries the writer has observed that furnace operators using stone produced at their own quarries manage to utilize much smaller sizes than are usually demanded where stone is purchased from independent quarry operators.

Regarding the upper limit of size, Maccoun¹⁸ claims that all stone should pass through a 6-in. ring, as larger lumps may go unburned even to the tuyere, wasting heat, and injuring the furnace lining by corrosion. Blast-furnace troubles have been attributed in some instances to irregularities in size of the limestone. In general, it may be said that uniform sizing improves the working of the furnace.

BASIC OPEN-HEARTH FLUX

The open-hearth process of making steel consists in melting pig iron and steel or iron scrap, and boiling the mixture generally with the addition of some very pure lump iron ore, until the carbon is reduced to the desired amount. A flux is added to the charge in the furnace mainly for the removal of phosphorus and sulfur. For a phosphorus content in pig iron not exceeding 0.25 per cent., additions of 6 to 12 per cent. limestone are considered good practice. When a pig iron with a higher phosphorus content is used, as much as 17 per cent. limestone may be charged. The phosphorus is oxidized to phosphoric acid, which unites with the lime to form calcium phosphate. The ability of a slag to take up phosphorus depends both on basicity and fluidity.

Fluorspar (CaF_2) is added because it increases the fluidity without decreasing the basicity. It is possible, however, to have the slag too fluid, for it then becomes active in attacking the dolomite lining. The more basic the slag, the higher its melting point; hence, the higher its temperature, the more lime it can absorb. An excessively high temperature is also destructive to the basic lining, as it may approach the softening point of the lining.

Choice between Limestone and Lime

Either lime or limestone may be used. When the flux is added in carbonate form the evolution of CO_2 makes the bath boil, insuring a lively reaction. Extra heat is required for calcination, but evidently no more than would be required for precalcination. Herty¹⁹ says that at some basic open-hearth furnaces flux charges consist of both limestone and lime, either as original charges of both or as a primary charge of limestone with subsequent additions of lime when it is found necessary to increase the CaO content of the slag. In some instances, the entire flux charge is of lime. This author claims that where lime is used the hot-metal (pig iron) content of the charge may be reduced, and thus the speed of the furnace may be increased.

It is stated by Baker²⁰ that the Dominion Iron Works, Sydney, N. S., uses lime made from a marble running less than 1 per cent. SiO_2 , purified

¹⁸ *Op. cit.*, 67.

¹⁹ *Op. cit.*, 592.

²⁰ D. Baker: Calcining Limestone for Use in the Basic Open-hearth Furnace. *Iron Age* (Apr. 21, 1904) 73, 6.

gas being used in calcining to keep down the sulfur content. Lime is used in place of limestone to reduce the time of heats. The Granite City Steel Works²¹ of the National Enameling and Stamping Co., at Granite City, Ill., has two rotary kilns each 8 by 110 ft., to burn lime for open-hearth furnaces. Evidently this company prefers burnt lime to limestone. Hamilton²² states that from a metallurgical standpoint limestone is preferable, but from an economic standpoint lime has certain advantages. He claims that furnace output may be increased about 20 per cent. when lime is substituted for limestone.

Effect of Impurities in Flux

In blast-furnace slag the proportion of $\text{CaO} + \text{MgO}$ to $\text{SiO}_2 + \text{Al}_2\text{O}_3$ is about 1 to 1, but with basic open-hearth slag this ratio is about 2.5 to 1. Hence if A equals the sum of per cents. of SiO_2 and Al_2O_3 in the fluxing stone, the bases ($\text{CaO} + \text{MgO}$) necessary to form a slag with these impurities will be $2.5A$, and the carbonates required will be $1.8 \times 2.5A$. The formula for determination of available carbonate is therefore $100 - (1.8 \times 2.5A + A)$, or $100 - 5.5A$. In comparing this with the general formula for available carbonate in blast-furnace flux, which reads $100 - 2.8A$, it is evident that impurities are much more detrimental in open-hearth than in blast-furnace flux. Thus a limestone with 2 per cent. impurity when used as blast-furnace flux would have an available carbonate content of 94.4 per cent., while if used for basic open-hearth flux it would have only 89.0 per cent. available carbonate. On this account specifications for open-hearth flux usually demand a limestone with a silica content not to exceed 1 per cent., and an alumina content not exceeding 1.5 per cent.

As the chief office of basic open-hearth flux is the removal of phosphorus, and as magnesium has a lower affinity than calcium for this element, dolomites or magnesian limestones are undesirable. The maximum permissible content of MgO is usually fixed at 5 per cent. The effect of magnesia on slag viscosity has already been discussed.

Size of Flux Stone

Great variation has been observed in the size of fragments. Some operators will take nothing under 5 in.; others use stone between 2 and 12 in. in size. Usually fines are excluded more rigidly by open-hearth operators than by blast-furnace men.

²¹ *Blast Furnace & Steel Plant* (Aug., 1921) 9, 467-8.

²² W. C. Hamilton: Open-hearth Furnace Slags. *Fuels & Furnaces* (Oct., 1926) 4, 1240.

Rate of Liquefaction of Flux

Limestones vary greatly in the rate at which the lumps are assimilated and become completely liquefied in the slag. Fragments of most well-consolidated limestones retain their original shapes, and are more or less firm and solid after complete calcination. Lime burners desire stone of this quality because it gives a high percentage of lump lime. Therefore, after the limestone lumps in an open-hearth furnace are completely calcined, they may still retain their original shapes. Limestones vary greatly in the rate at which such masses of lime dissolve or melt in the slag. This characteristic of the flux has a definite bearing on the proper size of fragments. Obviously if large masses of a slowly assimilated stone are used furnace operation will be retarded.

A loosely consolidated limestone that would completely disintegrate during the process of calcination would have the advantage of very rapid assimilation in the slag, but on the other hand such a stone would give excessive fines during the process of quarrying and crushing. It would appear that the furnace should not be supplied with large fragments of stone that is assimilated slowly in the melt. No definite data have ever been assembled on the rate of assimilation of various limestones in the open-hearth slag; nor, so far as I am aware, has a discussion of this problem ever appeared in print.

Use of Dolomite as Furnace Lining

In order to avoid rapid slag corrosion of furnace bottoms, basic open-hearth furnaces must be lined with basic material. The sides and roof are usually made of silica brick; the bottom is built up first with two or three courses of fire brick on the steel shell followed by two or more courses of magnesite brick, which are stepped up at the sides. Sometimes a course of chrome brick is inserted between the fire brick and magnesite brick. In some furnaces, the fire-brick courses are omitted. Occasionally a course of neutral chrome brick is inserted at the line where the magnesite-brick base joins the silica-brick walls.

The basic bottom is spread directly on the magnesite brick. Most basic bottoms are made of dead-burned grain magnesite, sometimes mixed with hot tar. A binder of 5 to 20 per cent. basic cinder is added. The grain magnesite is fused on in successive layers, building up the front and back walls well above the slag line. Commonly a wash heat of basic slag or roll scale is melted on and allowed to soak into the bottom. Formerly the preference was for Austrian magnesite but recently equally successful results are reported by operators using California, Washington and Canadian magnesites.

The difficulty of obtaining magnesite, together with its high price during the war period, led many operators to substitute burnt dolomite

for basic bottoms. For this purpose, dolomite should contain less than 1 per cent. SiO_2 , less than 1.5 per cent. combined Al_2O_3 and Fe_2O_3 , at least 35 per cent. MgCO_3 , and the remainder CaCO_3 . Dolomite is somewhat inferior to grain magnesite in that it cannot readily be made as dense and vitreous as magnesite and consequently disintegrates and floats up. Magnesite must either be imported or shipped from California or Washington, hence it is high priced; dolomite is of common occurrence, and is low priced. Many furnace operators who were forced to resort to dolomite for basic linings have voluntarily continued its use. Some operators report satisfactory results, for entire linings as well as for patching, from the use of burnt dolomites prepared in special ways and sold under various trade names. The general trend, however, has been to revert to magnesite, as it became available, for the major part of basic bottoms.

While admittedly inferior to grain magnesite, no basic material is found so generally suitable as burnt dolomite for minor repair work, as it is readily obtained at low cost, is sufficiently infusible for the purpose and at the same time sufficiently fusible to frit together and form a hard, mechanically strong bottom, which is not readily acted upon by the highly ferruginous and calcareous slags. Dolomite, therefore, is very widely used for patching. Small pits or holes in the bottom are repaired after each heat. It is estimated that 40 to 50 lb. of dolomite per ton of steel are needed for repair purposes.

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The writer desires to acknowledge many helpful suggestions from S. P. Kinney, T. L. Joseph and C. H. Herty, Jr., metallurgists of the Bureau of Mines.

DISCUSSION

G. C. STONE, New York, N. Y.—I have had a good many years' experience in this line of work, particularly in making zinc. When making slag the composition is an important point and I can say positively that the magnesia is much more effective than the lime as a flux.

When I started, we used as a flux half dolomite and half oyster shell. By paying attention to the composition we cut out the oyster shells and used dolomite alone with good effect and less cost. We needed a basic slag in that case; that is, basic as ordinarily classed. It was two of lime to one of silica or two of magnesia to one of silica.

Another point in using limestone is the temperature at which it burns and the time required to burn it. We were using two dolomites of exactly the same composition; one, a hard, dense, tough stone which burned very easily at a low temperature, the other a very highly crystalline marble, which even after heating to a red heat for 8 hr. contained a lot of undecomposed carbonate of lime. It was all right for the purpose for which we used it but it was of no use in the blast furnaces. In the blast furnaces we worked out a cut and dried proportion of limestone that gave good results.

I never could find any theory that gave the proper proportion of limestone until I learned of the work that Rigg had done in Australia with lead slags high in zinc oxide. He took a pot of the slag and covered it with sand so that it cooled very slowly, then he took sections of slag and examined them under the microscope, and they were the prettiest things I ever saw. Near the outside of the pot, where it had chilled very quickly, the development of the crystals could hardly be seen, but where it had cooled slowly three minerals showed: $\text{SiO}_2(\text{RO})$, $\text{Fe}_2\text{O}_3\text{FeO}$, $\text{Al}_2\text{O}_3\text{-ZnO}$. The two last both have the general formula $\text{R}_2\text{O}_3\text{RO}$. The slag was therefore a mixture of spinel and orthosilicate.

I next took the reports of the government on the manufacture of ferromanganese during the war, and they checked this composition perfectly.

The temperature at which limestone burns was gone into very carefully by the Carnegie company and a considerable difference was found in stones from different localities. Checking this carefully would often help a good deal; also, the study of the composition of the slags with the microscope would give much useful information.

J. T. MACKENZIE, Birmingham, Ala.—There is one use of dolomite which Mr. Bowles did not mention; that is, in slagging cupolas. About two months ago, we began to use dolomite in our cupolas and we find that only about four-fifths the amount of a well graded clean dolomite is needed to do the work of the limestone.

We find that a stone $\frac{1}{2}$ to 1 in. gives very much better results than the larger stone we used to use, but it is a great temptation to the foundryman to get the large stone because the small stone is so often dirty. Every car must be inspected when small stone is used, but I have no hesitancy in saying that flux in the cupola can be cut 30 per cent. by using $\frac{1}{2}$ to 1-in. limestone or dolomite, instead of the $2\frac{1}{2}$ or $3\frac{1}{2}$ -in. sizes, if the stone is clean.

L. F. REINARTZ, Middletown, Ohio.—This subject is of great importance to all open-hearth men, particularly from the standpoint of comparison between the effects of the use of limestone and burnt lime. A great many differences of opinion have arisen in regard to the two. The burnt lime will give a faster heat and also requires less pig iron, but the use of limestone has a tendency, on account of the boil generated by the carbon dioxide gas, to give a cleaner metal.

The size of the stone is a matter of controversy. We have always believed that it is possible to get the stone too large.

The statement has been made that the need for limestone is mainly for its fluxing action. We believe that the limestone has a greater function; that is, to form a protecting covering over the metal and prevent its overoxidation during the time the carbon is being worked down to the proper figure.

In years gone by, we had a great deal of difficulty in securing clean limestone, because the operators were not careful to strip the top off the limestone deposit, but in recent years they have been more careful and have not had nearly so much trouble.

Several years ago, we also had considerable difficulty because of slow heats in our open-hearth furnaces. We had not been analyzing the limestone regularly, and on investigation found that our purchasing department, without saying anything to us, had changed the source of supply and was buying limestone containing 5 to 8 per cent. magnesia instead of $1\frac{1}{2}$ or 2 per cent. The excess magnesia made the limestone stick on the bottom and this slowed up the time of our heats.

We have made a great many experiments with raw and burned dolomite and the prepared dolomitic products, as well as with the California magnesites, compared with the use of Austrian magnesites. In our practice, the Austrian magnesites give us by far the best results whenever we repair bad holes in the bottom. When there are small patches to be made on the slag lines, we use the prepared dolomite products. For the regular upkeep of the bank we usually use dolomite of a fairly uniform size.

G. C. STONE.—We once made some experiments on the fusing temperature of slags, as the result of an argument which I had with Esrey Johnson, in which we found that we were both right. As it turned out, he was speaking of acid slags made in the smelting of iron ore with charcoal and I was speaking of basic slags made in a blast furnace using coke and anthracite as fuel. First, we made up slags of perfectly pure material, then ground them fine and mixed them with a little dextrine and molded them into cubes around thermocouples. We heated these in a furnace that had a mica window, so that we could see what was going on and get the fusing point and also the point at which the cube dropped off the couple. With some of the slags, the softening point and flowing point were almost the same, while with others there was a difference of over 100° between them. We found that it made very little difference whether we used a silicate of lime or magnesia or a mixture of both, the fusing and flowing points were about the same as long as the proportion of bases to acid remained constant.

C. W. ANDREWS, Chicago, Ill.—Not very much has been said so far about usual blast-furnace practice, and I think it would be well to consider why we are using calcite or dolomite. If the slag is to be used for making cement, naturally calcite is wanted; if road material is to be made, dolomite should be used. The question of the purity of the stone is very important, but that again is a question of economics. What stone will give the cheapest net cost? In the Chicago district we are bringing stone down from Lake Huron in order to get a very pure calcite stone, and so it goes through the country. Each location has its particular problems which have to be solved to get the lowest cost of pig iron.

R. FRANCHOT, Washington, D. C.—In regard to the difference of effect of impurities in blast furnace and open hearth, which was brought out in the reading of the paper, it seems that perhaps the difference may not be so great when fuel consumption is taken into consideration. The evolution of CO₂ in the open hearth, as I take it, has no bearing upon fuel consumption, except that which is common to both practices—amount of heat it takes to burn the limestone. In the blast furnace, there is an additional effect of that CO₂ in solution loss, which appears to be quite marked. The solution loss would be a function of the CO₂ concentration and as that is added to by the CO₂ from the limestone, the effect, of course, is additional.

A One-ton Acid Open Hearth and Some Experimental Results

By C. E. MEISSNER,* CARTERET, N. J.

(New York Meeting, February, 1928)

THE need for a practical method of deciding upon new alloy steel analyses to widen its markets was the problem facing the Chrome Steel Works at the beginning of 1927. In addition to determining the physical properties of the alloys under consideration, it was necessary to test their value in service. Small melts of steel in a crucible, from which test specimens could be made, were insufficient to determine more than physical properties, therefore actual castings and ingots had to be made before the products could be placed in service. Furthermore, to save further experimental work, it was desirable that these heats should be made on a "pilot" basis; that is, actually duplicating regular open-hearth furnace practice. Therefore a one-ton (2000-lb.) acid open-hearth furnace was built.

FURNACE DESIGN

There are no special features in the design of this furnace. Standard acid open-hearth practice is followed, with the reportioning of the dimensions necessitated by its small size; notably, a considerably increased length in proportion to width in order to get proper flame propagation. After the first heat was made it was found that the checkers were insufficient. The checker chambers were increased in size and the checker openings were made much smaller. The furnace was started late in March, 1927, and made 65 heats. Experimental work was then stopped until the data accumulated could be worked up and summarized. The run was resumed in November and the furnace is still operating, having made at this writing 60 additional heats. For the last series of runs, there was some rebuilding of both the furnace itself and the checkers. Slag pockets were added. Fig. 1 shows details of construction; Fig. 2, the general appearance.

All designing was done by the operating and engineering staff. Construction materials were those available around the plant. The reversing valve is a standard butterfly type taken from an old furnace.

The slag pockets and checkers are cleaned by digging down to arched openings which have been bricked up.

* Development Engineer, Chrome Steel Works.

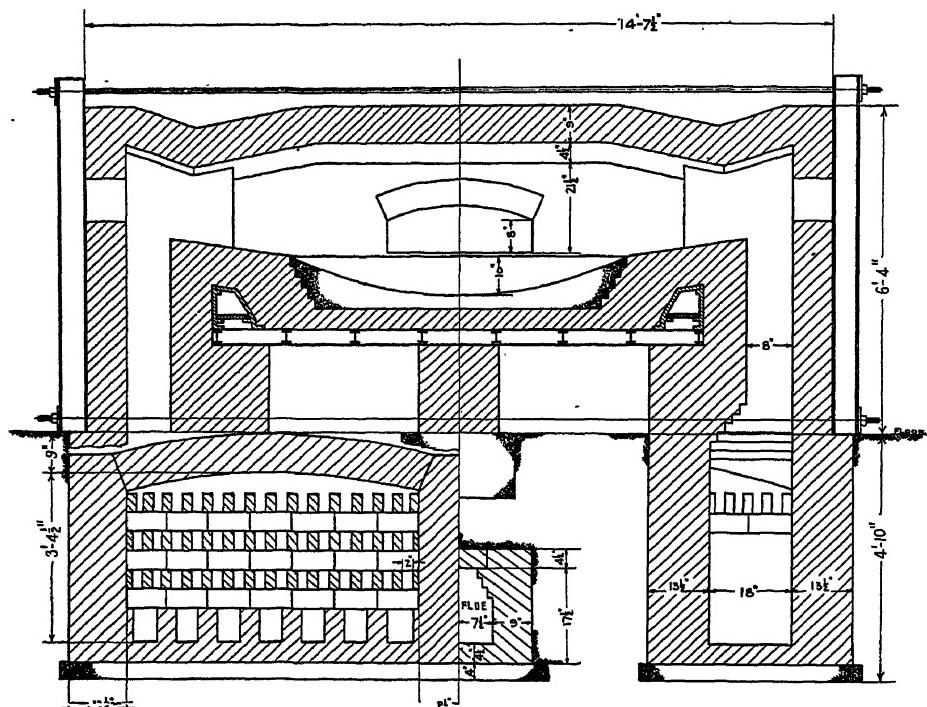
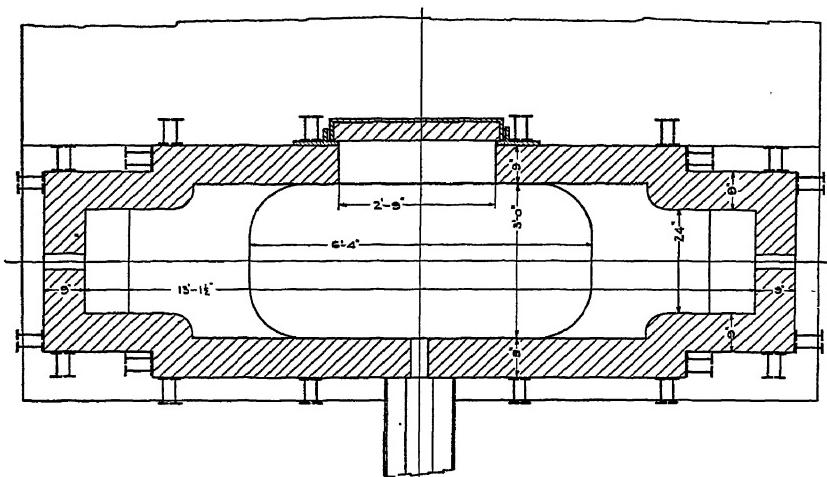


FIG. 1.—PLAN OF 1-TON ACID OPEN-HEARTH FURNACE.

Number of bricks required: 10,000 silica brick for furnace and checker chambers; 250 red bricks for pier.

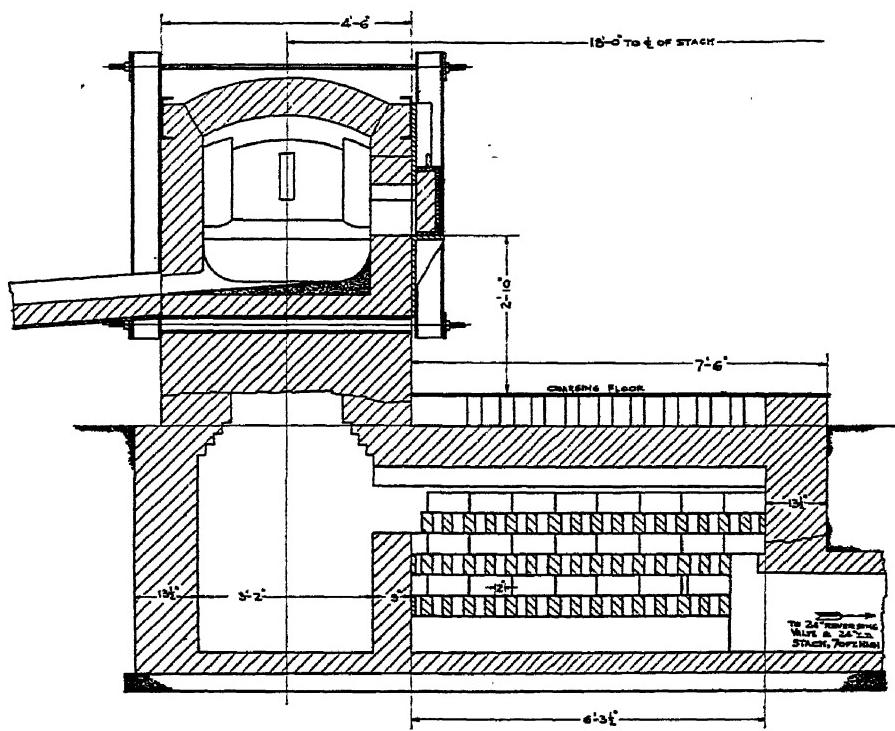
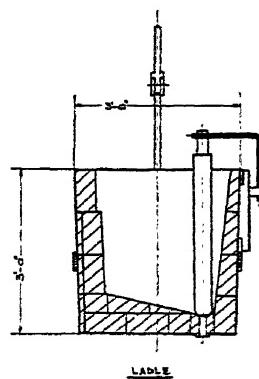


FIG. 1.—(Continued).

FURNACE PRACTICE

Bottom is made of a regular acid bottom sand, using a sand paddle. It needs little repairing and lasts about five heats. Charging is done by hand. The charge generally consists of about 1800 lb. of scrap and 200 lb. of pig. Alloy additions bring up the charge to about 2000 lb. of metal. The furnace loss is 6 to 10 per cent. Alloy losses are not greater than in a standard furnace. All alloys are added in the furnace except ferromanganese, which is sometimes added in the ladle.



FIG. 2.—ONE-TON ACID OPEN-HEARTH FURNACE.

The scrap used generally consists of locomotive tires and springs, rails and car wheels.

TABLE 1.—*Average Scrap and Pig Analyses*

	C	P	S	Si	Mn
Pig iron.....	3.85	0.035	0.04	1.85	0.63
Locomotive tires.....	0.50 to 0.85	0.05	0.05	0.15 to 0.35	0.75 max.
Locomotive springs.....	0.90 to 1.15	0.05	0.05		0.50
Rails.....	0.50 to 0.75	0.04	0.04	0.20 max.	0.60 to 0.90
Car wheels.....	0.65 to 0.85	0.05	0.05	0.15 min.	0.60 to 0.80

Melts can be made as high in carbon as desired. As our average analyses are high-carbon (0.65 to 0.90) alloy steels, a ratio of 10 to 20 per cent. pig to scrap is mostly used. Practice is to melt about 15 points higher in carbon than the final carbon desired and then work down before additions of alloys.

Ease of holding both heat and carbon is normal. Carbons as low as 0.04 have been attained and 0.06 carbon is quite easily reached.

Slags have been worked very successfully with iron reduced as low as 18 per cent. FeO. Two typical heats are shown on the accompanying heat records, giving details of alloy additions, slag-working analysis of

metal and similar details. One is high-carbon chrome molybdenum and the other a medium carbon with 3.5 per cent. chromium. Specifications are closely met, especially considering the great variety of heats made which varied from low-carbon steels to chrome irons with 27 per cent. chromium.

The furnace is oil-fired, using light, low-sulfur oil of 22° Be. The oil consumption is about 80 gal. per ton, which is double that normally used on the larger furnaces. This greater consumption is due to greater heat losses in this small unit. The oil is vaporized with compressed air at 100 lb. pressure. Standard burners are used. The flame is not more



FIG. 3.—TEAPOT POUR, 1-TON ACID OPEN-HEARTH FURNACE.

oxidizing than in the larger furnaces. Reversals are made every 15 minutes. Average time from charge to tap on normal heats is 4 hours.

Furnace life can only be estimated, but it is believed that the front and back walls will be the first to go at around 200 heats.

Metal temperatures during tapping have been noted as high as 3100° F. by optical pyrometers.

The furnace crew consists of a first helper with assistance from the regular pit gang for charging, tapping, etc.

Heats as small as 1000 lb. have been made in this furnace. Some of the steels have been very low in phosphorus and sulfur, as will be noted in Table 2.

LADLE

Small ladles previously used for an old crucible plant were rebuilt for this furnace. Bottom pour was found to be more satisfactory than the teapot pour shown in Fig. 3.

TABLE 2.—Some Experimental Results at Chrome Steel Works

	Analysis						Heat per 1000 lb.	Tensile Strength per 1000 lb.	Elongation per cent	Reduction of Area per cent	Brinell Hardness	Tensile	Shore	Heated to 50° F.	Heated to 100° F.	Heated to 150° F.	Cooling Medium	Reheated to 50° F.	Heated to 100° F.	Heated to 150° F.	Cooling Medium	Reheated to 50° F.	Heated to 100° F.	Heated to 150° F.	Remarks		
	C	P	S	Si	Mn	Cr																					
Cr-Mo steels.....	0.90	0.046	0.044	0.170	0.80	1.040	0.32	128	172	13	27	302	5	53	1560	2	air	1100	1	air	1100	1	air	1100	1	Rolled 1 in. square Rolled 1 in. square Rolled 1 in. square Treated as oversize tensile and load Casting coupon	
	0.88	0.047	0.045	0.301	0.631	1.01	0.23	124	174	14	31	236	5	55	1560	2	air	1100	1	air	1100	1	air	1100	1		
	0.90	0.037	0.042	0.410	0.451	1.360	0.30	140	174	11	32	304	8	53	1560	2	air	1100	1	air	1100	1	air	1100	1		
	0.90	0.022	0.037	0.411	0.451	1.360	0.30	95	156	9	9	302	2	49	1650	2	furnace	1100	1	air	1100	2	furnace	1100	2	Treated as oversize tensile and load Casting coupon	
	0.63	0.038	0.048	0.110	0.721	1.350	0.33	161	187	9	28	331	8	1650	1	air	1100	1	air	1100	1	air	1100	1			
	0.99	0.038	0.029	0.80	0.731	1.05	0.25	107	164	11	41	384	6	1650	1	air	1100	1	air	1100	2	furnace	1100	2	Treated as oversize tensile and load Casting coupon		
	0.99	0.038	0.029	0.80	0.731	1.05	0.25	89	158	7	9	302	4	52	1650	2	furnace	1100	1	air	1100	2	furnace	1100	2		
High-carbon low-chromium steels.	0.43	0.037	0.040	0.13	0.561	0.88		68	102	14	18	174	9	36	5	1650	2	air	1100	1	air	1100	1	air	1100	1	Casting coupon
	0.59	0.034	0.047	0.355	0.831	0.82		85	144	7	47	286	3	38	1	1650	2	As rolled	1100	1	air	1100	1	air	1100	1	Casting coupon
	0.59	0.034	0.047	0.355	0.831	0.82		73	132	12	13	235	3	38	1	1650	2	air	1100	1	air	1100	1	air	1100	1	
	0.70	0.055	0.064	0.38	0.64	0.79		89	128	3	62	1650	3	62	1650	1	air	1100	1	air	1100	1	air	1100	1		
2 to 8.5 per cent.	0.37	0.038	0.039	0.20	0.47	2.80		197	159	14	47	311	8	1650	1	air	1100	1	air	1100	1	air	1100	1			
chromium steels.	0.36	0.026	0.023	0.180	0.342	2.93		138	159	14	48	321	8	1650	1	air	1100	1	air	1100	1	air	1100	1			
	0.26	0.034	0.035	0.130	0.338	0.49	3.07	150	170	13	43	340	9	1650	1	air	1100	1	air	1100	1	air	1100	1			
	0.27	0.016	0.032	0.26	0.30	3.57		195	160	15	53	321	10	1650	1	air	1100	1	air	1100	1	air	1100	1			
2 to 8.5 per cent.	0.39	0.014	0.039	0.19	0.48	2.04		78	109	23	94	196	21	1650	1	air	1100	1	air	1100	1	air	1100	1			
chromium steels.	0.34	0.030	0.025	0.130	0.30	2.50		91	114	20	63	228	232	1650	1	air	1100	1	air	1100	1	air	1100	1			
	0.37	0.036	0.039	0.120	0.250	1.60	0.38	2	89	56	90	26	69	140	84	1650	1	air	1100	1	air	1100	1				
	0.21	0.032	0.036	0.130	0.330	0.49	3.07	88	110	22	67	228	24	1650	1	air	1100	1	air	1100	1						
	0.25	0.034	0.036	0.130	0.330	0.49	3.07	78	102	23	71	198	73	1650	1	air	1100	1	air	1100	1						
	0.27	0.016	0.032	0.26	0.30	3.57		165	172	14	49	320	22	1650	1	oil	1100	1	oil	1100	1	oil	1100	1			
	0.38	0.014	0.039	0.19	0.48	2.04		150	160	14	53	344	12	1650	1	oil	1100	1	oil	1100	1	oil	1100	1			
	0.42	0.017	0.039	0.26	0.46	2.31		156	164	14	53	340	13	1650	1	oil	1100	1	oil	1100	1	oil	1100	1			
	0.21	0.032	0.025	0.16	0.38	2.89		142	167	14	54	364	18	1650	1	oil	1100	1	oil	1100	1	oil	1100	1			
	0.27	0.016	0.032	0.26	0.30	3.57		117	125	20	66	269	16	1650	1	water	1100	1	water	1100	1	water	1100	1			
	0.21	0.032	0.025	0.16	0.38	2.89		110	125	18	63	269	16	1650	1	water	1100	1	water	1100	1	water	1100	1			
	0.27	0.016	0.032	0.26	0.30	3.57		117	133	19	61	269	11	1650	1	water	1100	1	water	1100	1	water	1100	1			
	0.21	0.032	0.036	0.33	0.49	3.07		146	180	11	27	364	6	1650	1	air	1100	1	air	1100	1	air	1100	1			
	0.27	0.016	0.032	0.26	0.30	3.57		135	160	15	53	321	10	1650	1	air	1100	1	air	1100	1	air	1100	1			
Cr-Mo and 3 per cent. chromium steels.	0.93	0.045	0.047	0.30	1.03	1.01	0.28	146	180	11	27	364	6	1650	1	air	1100	1	air	1100	1	air	1100	1			
	0.90	0.056	0.045	0.361	1.09	1.20	0.33	105	140	13	36	340	8	1650	1	air	1100	1	air	1100	1	air	1100	1			
	0.90	0.022	0.037	0.101	0.45	0.80	0.30	149	174	11	41	364	8	1650	1	air	1100	1	air	1100	1	air	1100	1			
	0.90	0.039	0.039	0.039	0.101	0.73	1.05	107	164	11	41	364	8	1650	1	air	1100	1	air	1100	1	air	1100	1			
	0.63	0.048	0.048	0.038	0.111	0.72	1.35	0.33	161	187	9	28	331	8	1650	1	air	1100	1	air	1100	1	air	1100	1		
	0.26	0.034	0.036	0.038	0.33	0.49	3.07	130	170	13	43	340	9	1650	1	air	1100	1	air	1100	1	air	1100	1			
	0.27	0.016	0.032	0.26	0.30	3.57		135	160	15	53	321	10	1650	1	air	1100	1	air	1100	1	air	1100	1			

Comparison of Cr-Mo and 3 per cent. chromium steels.

Rolled 1 in. rounds. Annealed at 1185 before machining test specimens

HEAT RECORD, OPEN-HEARTH DEPARTMENT, CHROME STEEL WORKS

Date 5-12-27	MATERIAL	Spec. Cr. Heat	Heat No. S0027	TIME
Charge:				
Low-phosphorus pig.....		200	7:55 First charge	
Springs.....		1800	9:00 Second charge	
			10:20 Charge melted	
Additions:				
Stirring rods.....		15	10:30	
Limestone.....		30	10:50	
Stirring rods.....		15	11:00	
FeSi, 50 per cent. Si.....		3 fines	11:30	
FeMn, 80 per cent. Mn, 6 per cent. C.....		5 fines	11:30	
Stirring rods.....		15	12:10	
FeSi, 50 per cent. Si.....		8	1:00	
FeMn, 80 per cent. Mn, 6 per cent. C.....		4	1:00	
FeCr, 70 per cent. Cr, 4 per cent. C.....		77	1:10	
FeMn, 80 per cent. Mn, 6 per cent. C.....		11	1:30	
FeCr, 70 per cent. Cr, 4 per cent. C.....		40	1:30	
Aluminum.....		1	1:38	
Total.....		2194		

Time of Operation:

	H.R.	MIN.
Charging time.....	1	5
Melting time.....	1	20
Time between final and ladle additions.....		17
Metal held in ladle.....		5
Pouring time.....		10
Tapping time.....		1.55 p. m.

History of Heat:

Color of slag.....	Dark yellow
Condition of slag.....	Heavy
Condition of metal tapping.....	Good hot side
Condition of metal in molds.....	Good heavy cream
Size ladle nozzle.....	Teapot ladle
Fracture test for solidity.....	Solid
Condition of furnace bottom.....	Good

Furnace Test:

TIME	C.
11:30.....	0.24
12:10.....	0.18
12:40.....	0.12
1:00.....	0.08
1:10.....	0.06

Analysis:

	C	MN	P	S	Si	Cr
Limits.....	0.22 to 0.28	0.50 to 0.70	0.04	0.04	0.20 to 0.30	3.40 to 3.60
Desired.....	0.26	0.60	0.04	0.04	0.25	3.50
Si fracture test.....					0.08	
Preliminary.....	0.06					
Final additions.....	0.24	0.74	0.015	0.030	0.17	3.64
Final.....	0.27	0.54	0.016	0.032	0.26	3.54

Total Weight:

	POUNDS
Castings.....	1139
Ingots.....	800
Skull.....	25
Spill.....	10
Losses.....	220
Total.....	2194

110 A ONE-TON ACID OPEN HEARTH AND SOME EXPERIMENTAL RESULTS

HEAT RECORD, OPEN-HEARTH DEPARTMENT, CHROME STEEL WORKS.—Continued

Date 8-16-27

Cr-Mo. Heat

Heat No. 80078

Charge:

MATERIAL	WT.	TIME
Low-phosphorus pig.....	400	7:30 First charge
Wheels.....	1600	9:00 Second charge 10:10 Melted

Additions:

Molybdenum.....	6	11:00
Limestone.....	40	11:30
Stirring rods.....	15	12:00
Stirring rods.....	15	12:40
FeSi, 50 per cent. Si.....	8	1:40
FeCr, 70 per cent. Cr, 5 per cent. C.....	30	2:30
FeMn, 80 per cent. Mn, 6 per cent. C.....	27	3:15
Aluminum.....	1	3:20

Total..... 2102

Time of Operation:

	HR.	MIN.
Charging time.....	1	30
Melting.....	1	10
Oil and air off, damper lowered.....		10
Tapping time.....		3:25 p. m.
Metal held in ladle.....		5
Pouring time.....		15

History of Heat:

Color of slag.....	Dark yellow
Condition of slag.....	Good
Condition of metal tapping.....	Good on hot side
Condition of metal in molds.....	Poured good in castings
Size ladle nozzle.....	1½"
Fracture test.....	Solid
Condition of furnace bottom.....	Good

Furnace Test:

TIME	C
12:00.....	0.97
12:25.....	0.92
1:00.....	0.87
1:40.....	0.84
2:15.....	0.81

Analysis:

	C	MN	P	S	Sr	CR	Mo
Limits.....	0.90 to 1.00	1.00 to 1.10	0.04	0.04	0.30	1.00	0.25 to 0.35
Desired.....	0.95	1.05	0.04	0.04	0.30	1.00	0.30
Si fracture test.....					0.15		
Preliminary.....	0.81						
Final additions.....	0.15	1.06	0.035	0.041	0.20	1.05	0.27
Final.....	0.92	1.10	0.037	0.040	0.41	1.10	0.30

Total Weight:

	POUNDS
Castings.....	1920
Skull.....	22
Spill.....	30
Losses.....	130

Total..... 2102

EXPERIMENTAL WORK

Some of the analyses and physical results are shown in Table 2. Several ranges of analysis have been worked on, which may be summarized as follows:

High-carbon steels with varying percentages of chromium from 0.30 to 1.00 per cent.

Chromium steels with carbon from 0.20 to 0.90 and chromium from 1.00 to 3.57 per cent.

Chromium-molybdenum steels with carbon 0.60 to 1.45 per cent., Mo., 0.25 to 0.35, Cr. from 0.80 to 2.50, and Mn from 0.60 to 1.25 per cent.

Chrome cast iron with carbon 2.75 per cent. and chromium 12 to 18 per cent.

Chrome iron with carbon 2.75 per cent. and chromium 23.0 to 27.0 per cent.

FIELD TESTS

The regular products of the Chrome Steel Works are crushing and grinding wearing parts. Therefore the principal experimental work has been directed to obtain extreme hardness with sufficient toughness for the requirements of the conditions. The results of these field tests are analyzed to determine further procedure. These are the high-carbon, 3 per cent. chromium and chromium-molybdenum steels.

The chromium cast irons are intended for furnace parts subjected to moderately high temperatures. This is a relatively inexpensive alloy and some tests to determine the value as compared to ordinary cast iron are now in progress.

The chrome iron is a more expensive alloy especially suited for resistance to abrasion, corrosion, heat and erosion. Various tests, such as skid rails in continuous furnaces, are in progress.

SUMMARY

The one-ton open hearth built and operated by the Chrome Steel Works has been entirely successful. It is a true "pilot" furnace, as all results may be duplicated on large-scale operation. Results of field tests on alloy steels have proved of invaluable assistance in the bettering of present products and in the opening of markets for new products.

DISCUSSION

L. F. REINARTZ, Middletown, O.—This is an interesting departure in experimental work. It is the first open-hearth furnace of this size that has been used in actual operation and also for experimental work. I have seen several larger furnaces but this is the first time I have heard of a furnace of 1-ton capacity. How were you able to control the slag so as to obtain just as good results on the small hearth as with a large one?

C. E. MEISSNER.—We have had no difficulty in that respect at all. The operation has been similar in every respect to a larger furnace. The only change made in the design was to lengthen the body, so that the operation of the furnace working down the impurities and adding the alloys has all been standard practice.

C. D. KING, New York, N. Y.—If, as Mr. Meissner says, it is truly a pilot furnace, it opens up a wide range of possible work for experimental purposes, not only along physical chemistry lines but also in heat loss determinations, design and operation of open-hearth furnaces. Today in large furnaces, by reason of the demand for steel, commercial requirements and operating conditions, it is rather difficult to set aside one specific furnace in the shop and devote that furnace to experimental work only. By means of a small furnace of this nature, it would be quite possible to run tests.

This furnace has 19 sq. ft. of hearth area, which would permit charging 2 tons. It would be interesting to develop the influence of fuel consumption with increased charge and the extra time necessary on increased charge by the same furnace. It would also be interesting to know by properly insulating the furnace which parts give best results. The problem could be nicely answered in the development of experimental furnaces of this same nature. The small size of the furnace would give quick comparisons, since all differences would be exaggerated.

L. F. REINARTZ.—Did you have any insulation on this furnace?

C. E. MEISSNER.—No insulation at all.

A. B. KINZEL, New York, N. Y.—The quality of the metal produced in this furnace is of interest. I have had occasion to test it, not only by the ordinary physical test but also by the microscopic and torch tests. It is very clean. If the plate or bar in question is melted at the edge or on the surface with a torch and the character of the melting carefully observed, when the material has inclusions, even though these be quite minute, they are easily visible on account of the light they emit on the surface. If there are small blowholes, the material melts with a spattering and spitting action. In the hands of an operator who has had experience with the oxy-acetylene torch, the quality of the metal can be determined.

L. F. REINARTZ.—Did you observe any difference in the iron oxide content of the slag?

C. E. MEISSNER.—No difference. We have had good "electric" slags. Those competent to judge have said they are as good as any they have seen.

A. L. FEILD, New York, N. Y.—One advantage of a furnace of this size, apart from what can be done in making experimental heats of unusual analysis, lies in the possibility of operating at extreme conditions, thereby showing the effect of variations in practice such as cannot be realized in a large furnace except at a prohibitive expense. The effect of extreme temperature on the various reactions may be readily studied.

The small size of the furnace is somewhat of a disadvantage in studying slags quantitatively, but it does not appear to be a serious one. Then, too, in the study of the physical chemistry of steelmaking, the question of the effect of hearth area is important. We have furnaces running from 15 to 20 tons up to 200 tons. Data on a 1-ton furnace would supplement the information obtained on the larger furnaces and be of very great value.

C. E. MEISSNER.—We are contemplating installing a brick of higher quality in order to make some of the materials which have a higher melting point. The chrome irons we have made are 27 per cent. chromium but 2.75 per cent. carbon, which is a considerably higher carbon than many of the ranges we would like to work with.

I would like to add that we have also built a larger body for this furnace which fits on the same checkers and is interchanged simply by picking up the bodies with an overhead crane. The dimensions of this larger body, which has a capacity of 5000 lb., are as follows: width, 5 ft. 6 in.; length, 14 ft. 0 in. The basin is 48 in. wide, 72 in. long and 15 in. deep. The checkers had to be increased to accommodate this larger body.

Rate of Carbon Elimination and Degree of Oxidation of the Metal Bath in Basic Open-hearth Practice

By ALEXANDER L. FEILD,* NEW YORK, N. Y.

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THE rate of elimination of carbon largely controls the time required to make a heat of steel by the basic open-hearth process and to an important degree determines the cost of refining. Practical experience has led to the generally accepted belief that the use of slags relatively high in iron oxide, such as are required to bring about rapid refining, leads to a certain sacrifice of quality in the product. As a consequence, a compromise must be made between the exceedingly slow rate of carbon drop which would correspond to the ideal case and the rapid rate which would best satisfy the condition of minimum cost. An increase in rate of refining necessarily implies an increase in the concentration of iron oxide dissolved in the metal. However, even for the infinitely slow rate that corresponds to slag-metal equilibrium, the metal would contain a certain definite concentration of dissolved iron oxide. It is a matter of great practical importance, therefore, to determine the quantitative relation between the minimum or equilibrium concentration of iron oxide in the metal and the higher concentrations which must actually obtain in practice.

The present paper is devoted to the development of certain equations, derived from the established laws of physical chemistry, which will enable this relation between rate of refining and the degree of oxidation of the metal bath to be computed from operating data. No attempt is made to exhaust the possibilities of this general method of treatment. In considering rate of refining, attention is mainly confined to rate of carbon elimination. However, the equations are of a more general nature and their application may readily be extended.

The results of the preliminary calculations given herein indicate that increased rate of refining may have a decided effect in increasing the concentration of iron oxide dissolved in the metal. The uncertainty which attaches to the calculated value for this relationship arises in part from probable errors in experimental data on which the calculations are based, and in part from the lack of complete or favorably disposed information on basic open-hearth practice.

When the relation between rate of refining and degree of oxidation of the metal has been more accurately established than has been done in the present paper, it will then become possible to consider what comprises

* Metallurgist, Union Carbide and Carbon Research Laboratories, Inc.

in any given case the most favorable refining rate and what particular percentage of iron oxide in the slag will lead to this favorable condition.

RÉSUMÉ OF PREVIOUS WORK

In a paper¹ presented in June, 1925, the writer attempted to treat of the kinetics of carbon, manganese, and silicon removal in the basic open-hearth process from the physico-chemical standpoint. In developing the theoretical principles set forth then, the writer assumed, among other things, that at any given temperature the percentage of iron oxide dissolved in the metal² prior to deoxidation was inversely proportional to the carbon content. In other words, it was assumed that equilibrium obtained between carbon and FeO in solution in the metal, in spite of the fact that carbon and FeO were subject to independent and continuous variation in their respective concentrations. This assumption, if correct, would be directly opposed to the generally accepted belief that speed of refining is an important factor in determining the state of oxidation of the metal prior to deoxidation; and would make it necessary to ascribe differences in quality of product exclusively to factors operating after deoxidation or at the time of deoxidation, where such differences could not reside in an effect due to temperature alone.

In a recent publication³ Herty and his associates have described in detail some of the experimental results which have been obtained in the course of their systematic investigations on the physical chemistry of steel-making. This publication, which contains a wealth of fundamental data of potentially great value to the steel industry, is not concerned with the question of rate of carbon elimination from the experimental standpoint, but does make certain statements relative to the practical side of basic open-hearth operation which depend for their correctness upon the validity of the assumption made by the writer in his former paper.

Originally, the writer did not believe that the percentage of dissolved FeO, which is a measure of the degree of the oxidation of the metal, is theoretically inversely proportional to the carbon content for a given temperature, but thought that this relationship expressed a very close

¹ Physico-chemical Phenomena from Melt to Ingots. *Trans. Faraday Soc.* (1925) 21, 255.

² The liquid metal, in addition to its content of dissolved FeO, generally holds a certain number of suspended, insoluble globules or non-metallic particles which in general contain iron oxide as a component. These undissolved, oxidized particles exert an entirely negligible effect so far as rate of oxidation of carbon, manganese, etc., is concerned. The analytical determination of FeO by known methods does not distinguish between these two modes of occurrence.

³ C. H. Herty, Jr., J. M. Gaines, Jr., B. M. Larsen, W. A. Simpkins, R. L. Geruso and S. P. Watkins: The Physical Chemistry of Steel-Making: The Solubility of Iron Oxide in Iron. *Bull. 34, Mining and Metallurgical Investigations*, Carnegie Institute of Technology, U. S. Bureau of Mines, and Advisory Boards (1927).

approximation to the condition which actually prevails. An equation was accordingly derived which expressed the relation at any given temperature between rate of carbon drop, carbon content, and FeO contents of metal and slag, which was of the form

$$-\frac{dx}{dt} = Kx_1wy(rw - y), \quad (\text{A})$$

where K was a "furnace constant" and the remaining symbols have the significance given in the table of nomenclature which follows. Since x_1y , the product of carbon and FeO, was assumed to be constant, equation (A) was in reality equivalent to

$$-\frac{dx}{dt} = K'w(rw - y), \quad (\text{B})$$

where K' is likewise a furnace constant.⁴

PURPOSE AND SCOPE OF THE PRESENT PAPER

A more careful consideration of the problem has led the writer to conclude that the above-mentioned assumption relative to equilibrium between carbon and FeO during the progress of refining may be inaccurate enough to lead to conclusions which are in error to an important degree. Accordingly, a development of physico-chemical principles is again attempted in the present paper in an endeavor to devise a method of treatment of open-hearth kinetics which is as rigorous and as free from assumptions as possible. Recourse is had to the ordinary mass-action law and to the theory of diffusion through interfacial films. A combined mass-action and diffusion equation is derived, from which it is possible to compute, among other things, the quantitative effect of rate of carbon drop on the FeO dissolved in the metal prior to deoxidation. An approximate method is also described for calculating rate of carbon drop. The equation employed in this calculation is compared with the corresponding equation of the writer's original paper and the degree of approximation and the limitations of both are pointed out.

THE PROCESS OF CARBON REMOVAL

The furnace atmosphere, which is always of a highly oxidizing character, is the ultimate source of the major proportion of the oxygen needed for reaction with carbon, manganese, silicon, and phosphorus dissolved in the metal bath, and hence the ultimate cause for the progression of the refining reactions. The oxidizing gases of the furnace atmosphere (chiefly CO₂ and H₂O, with or without a small proportion of free oxygen) react upon the metal in an indirect way through the slag as intermediary,

⁴ The constant product x_1y was introduced to give a function $y(rw - y)$ in the right-hand member of equation (A), which function has a maximum for $y = 0.5rw$. This device was employed for calculating y , the carbon-time curve in the case of the particular heat considered exhibiting a maximum for $-\frac{dx/dt}{K x_1 w}$.

or oxygen-carrier. These oxidizing gases, flowing over the upper slag surface, react with FeO in the slag and convert this lower oxide of iron to Fe_2O_3 , thereby enriching the upper slag surface in oxygen. Transfer of material from the upper to the lower slag surface occurs by virtue of the turbulence induced by the "drag" of the streaming furnace gases and the stirring action of the "boil," and to a minor degree by virtue of diffusion of iron oxide and the other slag constituents. As a result, Fe_2O_3 , the product of gaseous oxidation of FeO, is brought into contact with the metal bath at the lower slag surface, where it is reduced to FeO.

The slag, therefore, comprises the immediate oxidizing agent. It is, for practical purposes, insoluble in molten iron and actual removal of the oxidizable elements from the latter must be accomplished by diffusion or transfer of iron oxide from the slag to the metal across the slag-metal interface. Since FeO is soluble in molten iron and since Fe_2O_3 is converted into FeO upon coming into contact with molten iron, the above-mentioned transfer from slag to metal is a transfer of FeO alone. As has been pointed out by Herty and his associates, the percentage of Fe_2O_3 in the slag should be converted into its equivalent percentage of FeO in dealing with reciprocal relationships at the slag-metal interface. Hereafter, in referring to the iron oxide or FeO content of the slag it is to be understood that the equivalent FeO content of the slag is indicated; this is equal to the percentage of FeO plus 1.35 times the percentage of Fe_2O_3 by weight.⁵

In the case of interfacial diffusion of a solute from one solvent to another, such as that of FeO from slag to metal, a relatively simple theoretical treatment has been developed by previous investigators for the particular case where the solute concentration is at any given moment uniform, or substantially uniform, throughout each of the two solvents. This condition is favored by the turbulence and stirring action which characterizes the open-hearth bath. This theory of interfacial diffusion has been firmly established for ordinary solvents at ordinary temperatures and has already been successfully applied by Herty, Belyea, Burkart and Miller⁶ to the diffusion of SO_2 across the interface between slag and furnace gases. There are cogent reasons for applying it, if possible, to the problem of the diffusion of FeO across the slag-metal interface. It is possible to apply this theory to the problem in question provided FeC is not appreciably subject to stratification, either in the slag or in the metal. This condition is without doubt met except in those cases where

⁵ Here, as elsewhere in this paper, the use of molal concentration instead of percentage by weight would simplify the treatment. Other considerations, however have led the writer to use the customary weight percentages.

⁶ C. H. Herty, Jr., A. R. Belyea, E. H. Burkart and C. C. Miller: Some Factor Affecting Elimination of Sulfur in the Basic Open-hearth Process. *Trans.* (1925) 71, 512.

the slag exhibits such a high viscosity; *i. e.*, becomes so "thick" or pasty, that normal operation no longer prevails.

The interfacial diffusion theory is based on the fact that there exists on each side of the interfacial surface a very thin, stationary film, wherein it may be assumed that the concentration gradient of the solute is linear and transfer occurs exclusively by diffusion. The diffusional resistance at the interface is, therefore, equal to the sum of the diffusional resistances of the two contiguous films, which are, as it were, connected "in series." In a large number of cases the resistance of one of the films is so much greater than that of the other that consideration can be limited to it alone, the resistance of the more highly conductive film being negligible by comparison. Although proof is lacking, there is every reason to believe that in the present instance rate of diffusion of FeO across the slag-metal interface is, for practical purposes, entirely determined by the diffusional conductance of the slag film, which is exceedingly low by comparison with that of the metal film.

The FeO which enters the metal across the interface reacts with the oxidizable elements in accordance with the well-known chemical equations. Each part by weight of C, Mn, Si and P consumes during its oxidation 6.0, 1.3, 5.8 and 5.1 parts by weight of FeO, respectively. Oxidation of carbon consumes the major proportion of the FeO which enters the metal, and, during the finishing period of the heat, the rate of consumption of FeO by oxidation of Mn, Si and P is relatively, and frequently negligibly, small compared with the rate of FeO consumption by oxidation of carbon.

Oxidation of carbon proceeds by virtue of the reaction



The dissolved CO, which is a product of the above reaction, saturates the metal and thereafter escapes as gaseous CO at a pressure equal to the mean or effective hydrostatic pressure, which for convenience will be taken as equal to 1 atm. Since carbon elimination for pressures of CO below 1 atm. must depend entirely on outward diffusion of CO and can be neglected, it follows that the percentage of FeO dissolved in the metal is greater than that which would be in equilibrium with CO at a partial pressure of 1 atm., so long as carbon elimination with accompanying CO evolution is in progress. Unless, indeed, outward diffusion of CO is considered to be too slow to be of practical importance, there can be no such thing as equilibrium between carbon and FeO in the metal bath, excepting the hypothetical equilibrium at extremely low CO pressures where dissolved CO would by thermal dissociation be in equilibrium with the oxygen pressure of dissociated FeO at the slag-metal interface.

When carbon elimination ceases measurably to progress, the carbon and FeO dissolved in the metal are substantially in equilibrium with

CO at a pressure of 1 atm. and hence, for any given temperature, the product of carbon and FeO is equal to a constant, which will be designated as the equilibrium constant for the above-mentioned reaction. The values for this equilibrium constant have been calculated by Herty and his associates over a wide temperature range.

When carbon elimination ceases, the FeO in the metal is in distribution equilibrium with the FeO in the slag, or, in other words, for any given temperature the ratio of the percentage of FeO in the metal to the percentage of FeO in the slag is equal to a constant, which will be designated as the distribution constant.⁷ The values for this distribution constant have been determined experimentally over a wide temperature range by Herty and his associates. Values for the experimentally determined distribution constants and the calculated equilibrium constants, recalculated from the data of Herty to the particular units used in the present paper are given in Table 1.

TABLE 1.—*Equilibrium and Distribution Constants for Various Temperatures**

Temperature, Degrees C.	Equilibrium Constant = m	Distribution Constant = r
1524	0.044	
1536		0.0079
1562	0.037	0.0093
1592	0.026	0.011
1605	0.024	0.012
1660	0.021	0.015

* According to Herty et al.: *Op. cit.*

In general, if any two of the factors—carbon content, FeO content of the metal, FeO content of the slag, and temperature—are known, the remaining two may be calculated from the data of Table 1, provided the conditions are those of equilibrium prior to deoxidation.

THE DIFFUSION EQUATIONS

The equations which express the relation between rate of carbon drop, FeO content of the metal, and various other factors will now be developed. It is first necessary to consider the process of diffusion of FeO across the slag-metal interface.

⁷ This ratio, strictly speaking, is actually that of molal concentrations of FeO. The molal concentration of FeO in the metal is proportional to the actual weight percentage, and the same is true to a close approximation for the FeO in the slag. Herty and his associates express this ratio as that of molal fraction of FeO in the slag to weight percentage of "oxygen" (as FeO) in the metal. In the present paper, the weight percentage of FeO in the slag has been taken as equal to 120 times the molal fraction. The distribution ratio values here used were, therefore, derived by multiplying the values of Herty by 120/4.48 and taking the reciprocal of the product.

Table of Nomenclature

- Let x_1 = carbon in the metal, in per cent. by weight
 x_2, x_3 , and x_4 = Mn, Si, and P in the metal, respectively, in per cent. by weight
 y = FeO dissolved in the metal, in per cent. by weight
 w = effective FeO in the slag (FeO plus 1.35 times Fe_2O_3), in per cent. by weight
 m = equilibrium constant for the reaction $\text{C} + \text{FeO} = \text{CO} + \text{Fe}$ (for explanation, see section on Purpose of Paper)
 r = distribution constant (for explanation see section on Purpose of Paper)
 A = area of bath at level of slag-metal interface, in square feet
 M = weight of metal which comprises the metal bath, in pounds
 k = kinetic or rate constant for the reaction $\text{C} + \text{FeO} = \text{CO} + \text{Fe}$ (for explanation see next section)
 C = diffusion constant (for details see this section)
 p = oxidation ratio (for details see this section)
 W = quantity of FeO which diffuses from slag to metal per minute expressed in terms of per cent. by weight of the metal
 t = time in minutes
 $-\frac{dx_1}{dt}$ = derivative of x_1 with respect to t , or rate of carbon drop in per cent. carbon per minute. (The negative sign indicates a decrease of carbon with time)
 $\frac{dy}{dt}$ = rate of change in the FeO content of the metal, in per cent. FeO per minute
 $\frac{dx_2}{dt}, \frac{dx_3}{dt}$, and $\frac{dx_4}{dt}$ = derivatives of x_2, x_3 , and x_4 with respect to t , respectively
 $\frac{d^2x}{dt^2}$ = derivative of $\frac{dx_1}{dt}$ with respect to t , or rate of change of rate of carbon drop, in per cent. carbon per minute per minute.

Since the FeO which diffuses from the slag to the metal either remains dissolved in the metal or reacts with C, Mn, Si, and P,

$$W = -6 \frac{dx_1}{dt} - 1.3 \frac{dx_2}{dt} - 5.8 \frac{dx_3}{dt} - .51 \frac{dx_4}{dt} + \frac{dy}{dt}$$

$$\text{Let } p = \frac{-6\frac{dx_1}{dt} - 1.3\frac{dx_2}{dt} - 5.8\frac{dx_3}{dt} - 5.1\frac{dx_4}{dt}}{-6\frac{dx_1}{dt}}$$

Then, $W = -6p\frac{dx_1}{dt} + \frac{dy}{dt}$ (1)

It follows from considerations relative to interfacial diffusion through the stationary slag film, as already outlined, that

$$W = \frac{CA}{M} \left(w - \frac{y}{r} \right), \quad (2)$$

where C is the diffusion constant, which is numerically equal to the quantity of FeO, in pounds, which diffuses per minute across each square foot of interfacial area per unit difference in concentration of FeO between the upper and lower surfaces of the slag film. The concentration, or percentage, of FeO at the upper surface of the film is equal to w —the FeO content of the slag. That at the lower surface is equal to y/r —which is equal to the FeO content of a slag in equilibrium with the FeO in the metal. (The fact that the lower surface of the slag film is in equilibrium with the metal does not mean that equilibrium between slag and metal prevails, since a concentration gradient exists across the film and a diffusional transfer of FeO from slag to metal is in progress.)

Equating the right-hand members of equations 1 and 2 and transposing,

$$-6p\frac{dx_1}{dt} + \frac{dy}{dt} - \frac{CA}{M} \left(w - \frac{y}{r} \right) = 0 \quad (3)$$

Equation 3 is the general diffusion equation. The diffusion coefficient or "constant," C , depends on temperature and slag composition. The effect of composition on the value of C will be referred to later. For the present, C may be taken as a function of temperature alone. The value of C is not affected by rate of "boil," provided the agitation or stirring of the slag is sufficient to avoid stratification of FeO. Excessive "boil" probably has the effect of increasing the area of the interface; *i. e.*, in increasing the value of A . Since the terms A and C occur in equation 3 as a product, and since there is no obvious way to allow for the increase in A due to agitation, any value for C obtained by solving equation 3 or any equation derived therefrom will contain within it any effective factor of agitation, if such exists.

THE KINETIC EQUATION AND ITS DERIVATIVE

If the mean or effective CO pressure is taken during carbon elimination as equal to 1 atm., then

$$-\frac{dx_1}{dt} = kx \cdot y - k' \quad (3A)$$

when the kinetic constants k and k' are measures of the speed with which the reversible reaction $C + FeO = CO + Fe$ proceeds from left to right and from right to left, respectively. By definition, $k'/k = m$, hence,

$$-\frac{dx_1}{dt} = k(x_1y - m) \quad (4)$$

For any given value of carbon content and temperature, the term x_1y is a measure of the actual concentration of FeO dissolved in the metal and m of the concentration which corresponds to equilibrium. It is, therefore, apparent that equation 4 is in effect a simple expression of the well-known law that rate of reaction is proportional to distance from equilibrium.

From equation 4,

$$y = \frac{m}{x_1} - \frac{1}{kx_1} \frac{dx_1}{dt} \quad (5)$$

Equations 4 and 5 express a fundamental relation which exists between carbon content, FeO in the metal, rate of carbon drop, and temperature, since the constants m and k are functions of temperature alone.

Upon differentiating equation 4 with respect to t , there is obtained, after transposing terms,

$$\frac{dy}{dt} = \frac{-y}{x_1} \frac{dx_1}{dt} - \frac{1}{kx_1} \frac{d^2x}{dt^2} \quad (6)$$

(Attention is called here to the fact that it is not permissible to write down the relation

$$-\frac{dy}{dt} = j(x_1y - m)$$

corresponding to equation 4, where j is a kinetic constant, since this is precluded by the fact that the FeO content of the metal is being continually replenished by diffusion from the slag.)

THE COMBINED DIFFUSION AND KINETIC EQUATION

Substituting in equation 3 the values of y and $\frac{dy}{dt}$ given by equations 5 and 6, respectively, there is obtained a general equation which represents a combination of diffusion and kinetic terms and from which terms relating to the FeO content of the metal are absent. The equation in question is the following:

$$-6p \frac{dx_1}{dt} - \frac{mdx_1}{x_1^2 dt} + \frac{1}{kx_1^2} \left(\frac{dx_1}{dt} \right)^2 - \frac{1}{kx_1} \frac{d^2x}{dt^2} - \frac{CA}{M} w + \frac{CAM}{Mrx_1} - \frac{CA}{Mkrx_1} \frac{dx_1}{dt} = 0 \quad (7)$$

Equation 7 is an ordinary differential equation of the second order and second degree, has variable coefficients, and is apparently of a type

difficult of solution, if indeed a general solution is possible. However, it does not appear that integration of equation 7 is a necessary requirement for its practical application to the basic open hearth, and, in fact, the equation as it stands in its present differential form has certain advantages.

The values for $\frac{dx_1}{dt}$ and p which express or involve oxidation rates can be determined directly by chemical analysis of a series of samples taken from the metal bath at known intervals during the progress of the heat. One method of deriving $\frac{dx_1}{dt}$, $\frac{dx_2}{dt}$, $\frac{dx_3}{dt}$ and $\frac{dx_4}{dt}$ is to plot percentages of C, Mn, Si and P as ordinates against time in minutes as abscissas, and then to determine the slopes of the resulting curves graphically at any selected time. The derivatives in question are numerically equal to the slopes of the respective curves. The second derivative, $\frac{d^2x}{dt^2}$, may be determined, when necessary, by plotting values for $\frac{dx_1}{dt}$ as ordinates against time as abscissas and again measuring the slope of this derived curve. For those portions of the carbon-time curve which are linear, the value of $\frac{dx_1}{dt}$ is, of course, a constant and that of $\frac{d^2x}{dt^2}$ is equal to zero.

Another method of determining these quantities consists in deriving the equation of the carbon-time curve for the period under consideration and differentiating this equation. The values of x_1 and w are obtained from the ordinary analysis of the metal and slag, respectively. The values of A and M are known from data on the design of the furnace hearth and from charge weights, respectively. Temperature may be measured optically and the proper values assigned to m and r (see Table 1).

There remain, however, among the quantities involved in equation 7 two whose values cannot be determined from ordinary operating or analytical data, or from known physico-chemical constants. These two quantities are k and C ; the kinetic constant and the diffusion constant, respectively.

Now m , r , k , and C are functions of temperature and, in general w , x_1 , p , $\frac{dx_1}{dt}$, and $\frac{d^2x}{dt^2}$ are functions of time. The quantities A and M are substantially independent both of time and temperature after the charge has been melted down. Since equation 7 contains two unknown quantities, k and C , for the calculation of which two simultaneous equations are required, it follows that the two sets of known data substituted in equation 7 for the purpose of constructing the two simultaneous equations must refer to a known and constant temperature.

The only published record of a basic open-hearth heat which is sufficiently complete and accurate to serve as a basis for calculating k and C is that in a paper by Keats and Herty.⁸ The value of A , the area of the bath, is not reported, but in a private communication from Doctor Herty this value is given as about 450 sq. ft.

The ideal condition in practice for supplying data to be used in solving equation 7 for k and C would be represented by a period during the finishing stage, reasonably removed from any ore additions, when the carbon content of the metal is dropping at a uniform or gradually varying rate. Unfortunately, the particular heat described by Keats and Herty does not exhibit such a condition, although it is certain that heats do frequently exhibit this favorable condition. The most favorable condition prevailed during the interval from 7:21 p. m. to 7:52 p. m. when the carbon fell from 0.342 per cent. to 0.222 per cent. The final ore addition (1800 lb.) was made at 7:05 p. m., high-carbon ferromanganese was added at 7:52 p. m., and the heat tapped at 7:55 p. m.

This particular portion of the carbon-time curve is defined by the following coordinates:

TIME, P. M.		x_1
7:21	0	0.342
7:35	14	0.268
7:52	31	0.222

Substituting these values of t and x_1 in the power-series equation, $t = a + bx + cx^2$, and solving for a , b , and c , it is found that $a = 201$, $b = -1095$, and $c = 1483$. Hence, the equation of this portion of the carbon-time curve, referred to 7:21 p. m. as the origin of coördinates, is equal to $t = 201 - 1095x_1 + 1483x_1^2$. Differentiating this equation, $\frac{dx_1}{dt} = \frac{1}{-1095 + 2966x_1}$, and $\frac{d^2x}{dt^2} = \frac{2966}{(-1095 + 2966x)^3}$. During this same period the temperature was substantially constant at 1580° C. and, due to the negligibly small rate of drop of Mn, Si, and P, the value of p may be taken as unity. The two sets of values for substitution in equation 7 are the following:

	I	II
x_1	0.268	0.222
$\frac{dx_1}{dt}$	-0.00333	-0.00229
$\frac{d^2x}{dt^2}$	0.00011	0.000035
w	17.59	15.55
r	0.0102	0.0102
M	245,000	245,000
A	450	450
p	1	1

⁸ J. L. Keats and C. H. Herty, Jr.: Elimination of Metalloids in the Basic Open-hearth Process. *Trans. (1926)* **73**, 1079.

From Table 1, it will be observed that the value of m , the calculated equilibrium constant, for a temperature of 1580° C. is equal to 0.0303. Now when this value of m and the values of the other quantities given in the columns above are substituted in equation 7 and the two resulting equations solved for k and C , values are obtained which are imaginary, that is to say, they involve the square root of a negative quantity. Examination has shown that real values for k and C are obtainable only when the value assigned to m is smaller than the above-mentioned calculated value of 0.0306. Actually, there are reasons for believing that the calculated values of m given in Table 1 are too high, quite apart from the reason that these values do not appear to be consistent with equation 7 and the data of the Keats and Herty heat. If it is true that a steel or "iron" containing as low as 0.015 per cent. carbon can be produced under a slag containing 48 per cent. FeO at a temperature of 1650° C., then the value for m at this temperature would be equal to 0.007 instead of 0.0206, as given in the table. In other words, the previously calculated value would appear to be considerably higher than it should be. The value of 0.0102 will be arbitrarily assigned to m for a temperature of 1580° C., instead of the value of 0.306 indicated in Table 1, in order to permit equation 7 to be solved for k and C .

Upon substituting the above values in equation 7 and solving the two resulting simultaneous equations, the following values for k , $\frac{CA}{M}$, and C are obtained:

$$k = 0.139; \frac{CA}{M} = 0.00368$$

and

$$C = 2.00$$

Since the solution of equation 7 involves differences between terms of the same order of magnitude, experimental errors in determining x , w , $\frac{dx_1}{dt}$, and p , as well as temperature, are reflected in the calculated values of k and C in a magnified degree. For this reason, it is important to accumulate additional records similar to that given in the paper of Keats and Herty in order to make a more reliable calculation possible. At the same time, a recalculation of m , from data which correspond to as close an approach to equilibrium conditions as possible, should be undertaken. The determination of the temperature coefficients of k and C would also be desirable and this would involve accurate data for practices which differ as widely as possible in finishing temperature.

RELATION BETWEEN RATE OF CARBON DROP AND DEGREE OF OXIDATION OF THE METAL

Assuming for the time being that the data used in the calculation of k and C are accurate enough for practical purposes, and therefore that the

value of 0.139 for k at 1580° C. is reasonably correct, it becomes possible to calculate how the FeO content of the metal varies with rate of carbon drop for the particular operating temperature of 1580° C. by employing equation 5 and assigning various values to x_1 and $\frac{dx_1}{dt}$.

The proportional increase in FeO due to rate of carbon drop, over and above the equilibrium value, is an inverse measure of the degree to which furnace practice approaches the ideal. At equilibrium the value of y , the FeO content of the metal, is equal to m/x_1 . Otherwise, its value is equal to the right-hand member of equation 5, or to $\frac{m}{x_1} - \frac{1}{kx_1} \frac{dx_1}{dt}$. The proportional increase due to rate of carbon drop is, therefore, equal to $-\frac{1}{mk} \frac{dx_1}{dt}$. A value for this proportional increase of 0.25, for instance, indicates that the metal contains an excess of FeO over and above the theoretical minimum which is equal to 0.25 times this theoretical minimum, or equilibrium, value. As is to be observed, the value of this proportional increase of FeO due to carbon drop is determined entirely by the temperature functions m and k and by rate of carbon drop, and is independent of carbon content.

In the particular case of the Keats and Herty heat referred to above, where the rate of carbon drop was equal to 0.00333 at a carbon content of 0.268 per cent. and a temperature of 1580° C., the metal contained an excess of FeO over and above the equilibrium value which would be calculated to be equal to $\frac{0.00333}{0.0102 \times 0.139} = 2.35$ times this latter value.

In other words, the metal would contain 3.35 times as much FeO as would be calculated on the assumption that the FeO or "oxygen" content of the metal depended entirely upon carbon content and temperature. (As before, an arbitrary value of 0.0102 for m is used in the calculation.) The FeO content of the metal would be 0.127 per cent. as against the equilibrium value of 0.038 per cent.

In accordance with the view that equilibrium obtains between carbon and FeO during the progress of a heat, it would necessarily follow that the percentage of dissolved FeO and the degree of oxidation of the metal bath would increase gradually and continuously as the carbon was removed. If, on the other hand, the concentration of dissolved FeO in the metal largely depends on rate of carbon drop, as has been indicated above, a retardation or slowing-up in rate of carbon drop, due to reciprocal relationships between temperature and composition of metal and slag, should correspond to a decrease in the FeO content of the metal if such retardation is of sufficient magnitude, in absence of any deoxidizing additions. In other words, an actual "shaping up" of the metal bath so far as its degree of oxidation is concerned would be possible, and this

would appear to be in accord with the commonly held belief of operating men. In a case where the FeO content of the slag is not too high for the carbon content at which the heat is to finish, this "shaping up" of the metal would automatically accomplish itself if ore additions are withheld toward the end of the heat, provided, of course, normal operating conditions are maintained.

THE FACTORS WHICH DETERMINE RATE OF CARBON DROP

Equation 7 cannot in general be employed for the purpose of predicting rate of carbon drop, since it contains a second derivate, $\frac{d^2x}{dt^2}$. It has been the writer's observation that in a large proportion of cases the carbon-time curve is substantially a straight line over a considerable part of the working and finishing periods. When this condition holds, the second derivative term is equal to zero and equation 7 may be employed for calculating $\frac{dx_1}{dt}$. Upon transposing terms and putting $\frac{d^2x}{dt^2}$ equal to zero, this equation yields the following when solved for $\frac{dx_1}{dt}$:

$$\text{Rate of carbon drop} = \frac{dx_1}{dt} = \frac{(B_1 - B_2)}{2B_3} \quad (8)$$

where

$$B_1 = 6pkx_1 + \frac{km}{x_1} + \frac{CA}{Mr}$$

$$B_2 = B_1^2 - 4B_4B_3$$

$$B_3 = -\frac{1}{x_1}$$

and

$$B_4 = \frac{cAk}{M} \left(wx_1 - \frac{m}{r} \right)$$

If consideration is limited to approximately linear carbon-time curves and to reasonably high carbon contents, above 0.10 per cent. for instance, no very appreciable error is introduced by assuming that $\frac{dy}{dt}$ in equation 3 is relatively small by comparison with $-6p \frac{dx_1}{dt}$. For this condition, equation 7 is considerably simplified, and the equation which governs rate of carbon drop becomes

$$-\frac{dx_1}{dt} = \frac{c(bx_1 - 1)}{(b'x_1 - 1)}, \quad (9)$$

where

$$b = \frac{wr}{m}$$

$$b' = \frac{6pMkr}{CA}$$

and

$$c = km.$$

Equation 9 is readily integrated, and in integrated form represents an equation by means of which the time required for the carbon content to fall from any initial value x'_1 to any lower value x_1 may be calculated, provided w , p , and temperature remain substantially constant over the interval in question.

$$\text{Time (minutes)} = \frac{b'(x'_1 - x_1)}{b} - \frac{2.3(b - b')}{b^2} \log \frac{(bx'_1 - 1)}{(bx_1 - 1)} \quad (10)$$

By assuming that $\frac{dy}{dt}$ is relatively small under the conditions mentioned above, equation 3 reduces to

$$-\frac{dx_1}{dt} = \frac{CAr}{6pM} \left(w - \frac{y}{r} \right), \quad (11)$$

which is of a form similar to that of equation B and would be identical therewith provided $Kw = \frac{Car}{6pM}$. This equality is not conceivable unless C , the diffusion constant, is proportional to w , the FeO content of the slag. The diffusion constant has so far been considered as a function of temperature only, and it is known that one of the chief effects of temperature on C is due to its effect on slag viscosity. But slag viscosity at any given temperature is to a considerable extent affected by slag composition, and in particular by the FeO content of the slag. If at a given temperature the value of C is inversely proportional to slag viscosity, as it is actually believed to be, and if viscosity is inversely proportional to the FeO content of the slag, then equation B is applicable to the same conditions as equations 9 and 10. While slag viscosity is known to increase with decrease in FeO content of the slag, other things being equal, there is nothing known at present about the quantitative relationships involved.

The treatment of the present paper, so far as it has been possible to extend it, is applicable to a basic open-hearth bath wherein the FeO which diffuses into the metal, and thereby brings about oxidation of C, Mn, Si, and P is derived from a molten slag of uniform composition. Variations in the FeO content of the slag which may normally occur from point to point in the bath do not affect the methods of calculation appreciably, provided the value of w employed in the equations represents the average value. The method of treatment, however, is not applicable to the refining process for those intervals of the heat which immediately follow any substantial addition of lump ore. Such lump iron ore, having a greater density than the slag, and also requiring a certain interval of time to fuse and become disseminated in the slag, first settles through the slag layer and comes to rest at the slag-metal interface, where a portion of the surface of the lumps or their undisseminated semi-fused residues are in rather intimate contact with the metal for an appreciable length of time. These ore lumps and their residues, presenting to the metal a reactive

surface composed of substantially pure Fe_2O_3 , bring about a certain increase in oxidation rate for the bath as a whole. An investigation of the effect of ore additions on rate of carbon drop would yield valuable results and would extend the scope of application of the equations of the present paper. It is not believed that the effect of ore additions by virtue of a direct-contact action on the metal, as distinguished from the effect in increasing the FeO content of the slag—when such increase actually occurs—extends over a period longer than about 20 min. following the addition.

While reference has been made throughout the paper to the temperature of the bath, it must be recognized that at the present time it is possible only to measure the temperature of the exposed slag surface, using an optical pyrometer. The temperature of the metal cannot be measured until the heat is tapped and the free surface of the metal is exposed to view. One of the most urgent needs of the open-hearth operator is some reliable and reasonably accurate means of measuring the temperature of the metal as it lies beneath its blanket of slag. The question, too, of what particular temperature to employ in evaluating the temperature functions m , k , C , and r should be considered. In general, the temperature of the slag differs from that of the metal and is usually somewhat higher. The temperature of the interface will lie between that of the slag and metal, and, in view of the relatively high thermal diffusivity of the metal will be very close to the temperature of the metal, regardless of slag temperature. The temperature of the metal determines m and k ; the temperature of the interface determines r , and, together with slag composition, determines C . The low total heat capacity of the slag, its low thermal conductivity, and high viscosity cause it to respond with relative rapidity to variations in rate and distribution of heat supply from the furnace gases, particularly the slag surface. For this reason, the observed temperature of the slag surface is a rather unreliable measure of the temperature of the metal and of the interface.

It does not appear that any method has been devised for distinguishing by chemical analysis between the FeO which was originally dissolved in the liquid metal and that which was simply held in suspension as ferrous silicate. If, therefore, an experimental determination of the total FeO content of a metal sample taken during the progress of a heat shows a percentage higher than that calculated from the equilibrium constant, m , it would be difficult to maintain that this implied an effect due to rate of carbon drop, unless the difference between the two was relatively large or unless the metal sample contained a negligibly small content of silicated non-metallics. On the other hand, if such an experimentally determined value were larger than the calculated equilibrium value by an inappreciable amount, it would definitely show that in the particular case in question rate of carbon drop had no effect on the dissolved FeO in the metal.

As has been pointed out above, the calculated equilibrium constants which have been proposed by Herty and his associates are probably too high, so that it would be necessary first to establish these values more accurately.

SIGNIFICANCE OF THE RESULTS OBTAINED

It is believed that the results obtained in the present paper, in the direction of developing certain new theoretical principles relative to basic-open steel refining and of indicating briefly the manner of their application to practice, point definitely to several general conclusions of importance. The first conclusion is that there is no conflict between theory and practice, and that the commonly accepted beliefs and ideas, so far as they go, contain the germ of truth, in most cases at least. However, the next conclusion, which inevitably follows from a careful consideration of the complexity of the physico-chemical process which comprises basic open-hearth refining, is that it can only be through the application of a perfectly elaborated theory of the process, confirmed by and based upon accurate experimental measurements, that the metallurgical and economic factors involved will be brought within intelligent understanding. The ability of a science to predict quantitatively is a measure of its degree of perfection, and prediction requires an adequate theory and the necessary fundamental data. It has been to this general end that the present paper is devoted. If engineering be defined as the application of known scientific theories and data to a practical purpose, then the metallurgical engineering of the steelmaking processes must inevitably come to be regarded as applied physical chemistry. It is believed that this time is nearer than is generally believed, if indeed it is not already at hand.

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To Dr. Charles H. Herty, Jr., supervising metallurgist, Pittsburgh Experiment Station of the Bureau of Mines, who called attention to several errors in the mathematical equations and calculations of the original manuscript, the writer wishes to express his sincere thanks for his careful reading of the manuscript and for his invaluable assistance.

DISCUSSION

C. H. HERTY, JR., Pittsburgh, Pa.—This paper is based on the premise that given a layer of slag and metal there is FeO in the slag which is diffusing into the metal. The carbon reacts with FeO, giving CO and metallic iron.

The author simply states that the FeO diffusing into the metal is equal to that being reduced by carbon plus any increase of FeO dissolved in the metal during the period of time under consideration. He also states that the more rapid the rate of carbon elimination the greater the excess of iron oxide dissolved in the bath over that required to satisfy the equilibrium conditions of the reaction.



The amount of overoxidation, as calculated from the equations in this paper, depends entirely on the values of the constants obtained, and these depend on whatever value of m is assumed to be correct.

Mr. Feild has three constants in the equation: m , C and k . The m is essentially equal to the product of carbon times FeO; that is the equilibrium constant when CO is given off at atmospheric pressure. C is equal to the diffusion constant, which means that for a unit concentration of FeO in the slag and unit area, so much will be diffused into the metal; k is equal to the rate constant. If there is unit concentration, carbon or FeO is eliminated at a given rate. The whole question of oxidation depends on the value selected for m . That is the question with this particular paper. Unfortunately, nobody knows the correct value of m .

In some work we did last year⁹ we estimated the value of m at 0.03 from open-hearth data. We admitted at the time we did it that m was too high because we were dropping carbon slowly.

Mr. Feild has arbitrarily taken m equal to 0.01. That is a pretty big reduction from 0.03. I am sure 0.03 is too high but how much I do not know, but I do not believe m is as low as 0.01. If 0.01 is used as this constant, the figure obtained is approximately three times as much iron oxide dissolved in the metal as might be expected if equilibrium existed in the metal.

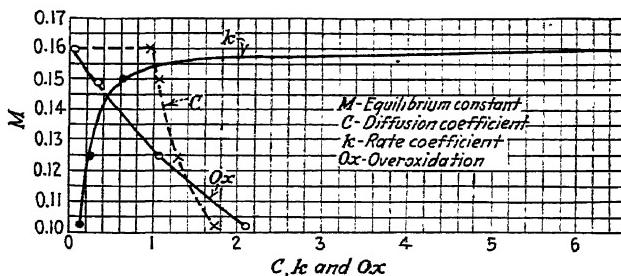


FIG. 1.—VARIATION IN C , K AND Ox WITH VARIATION IN m . WHEN $m = 0.0160$ DIFFUSION IS CONTROLLING AND OVEROXIDATION OF BATH APPROACHES ZERO.

I thought it might be interesting to pick some other values of m . Fig. 1 shows the results of that calculation. In order to make diffusion controlling and overoxidation low, the value of C has to be low and k high. That makes the rate of reaction fast and the diffusion slow. The author has taken 0.01 and he finds the oxidation is about twice as much as one would expect. On the other hand, if the value of m is increased, k increases rapidly.

At $m = 0.016$, the equation becomes indeterminate. If m is equal to 0.016, zero overoxidation would result and diffusion would be so slow that carbon would eliminate FeO as fast as it entered the metal. I believe overoxidation of the metal is low.

With a high iron oxide slag, which according to Feild would give a high overoxidation, there would be trouble whether or not there was overoxidation. As soon as a

⁹Solubility of Iron Oxide in Iron. Carnegie Inst. of Tech. Bull. 34 (1927).

bath is killed, nonmetallics form just as if it had been overoxidized. The only way to prove it is to get samples from open-hearth furnaces, working under different conditions. The important point to be proved is whether the bath is contaminated excessively before or after deoxidation. The proper method of treating the steel should be determined by knowing the time at which most contamination occurs.

L. F. REINARTZ.—Mr. Feild speaks of determining the overoxidation, checking it up by the iron oxide in the metal. It is difficult to determine iron oxide in the metal in a rapid way but you can get it in the slag quite rapidly. What would an open-hearth man do in that case?

A. L. FEILD.—If we can determine accurately once and for all the values of the equilibrium constant, m , for different temperatures, we need never determine it again. The question of what value to employ in our calculations will then become simply one of measuring metal temperature. That is why Dr. Herty stressed the importance of determining the equilibrium constant. It should be mentioned here that the value of 0.03 for m which Dr. Herty uses was calculated from data on heats which probably did not reach complete equilibrium. When I first solved equation 7 for k and C , using $m = 0.03$, I obtained results which could only refer to imaginary conditions. It was some time before it occurred to me that if equation 7 is correct, the value of m cannot exceed a certain maximum value, which in this instance is less than 0.03. The value of 0.01 was arbitrarily selected, although it has its basis in deductions made from approximately correct data on open-hearth practice.

L. F. REINARTZ.—How will a practical man use the equation?

C. H. HERTY, JR.—If there are no t constants in the expected rate of carbon drop, analyze the slag for FeO 1 hr. or so before tapping and the gas oxidation can be controlled. When the steel has the desired carbon it will have as small iron constant as possible. Analyze the slag, then, by the use of tables calculated from the constants, determine the quantity of ore which must be added to finish at a certain carbon in a given time.

L. F. REINARTZ.—What effect will slag volume have?

C. H. HERTY, JR.—I do not believe it will have very much effect in the ranges run in the shops. Different shops use different practices. It will be necessary to modify the additions according to the slag volume. That will be worked up in tables. The iron oxide in the slag can be controlled.

L. F. REINARTZ.—The author says that all the iron present was iron oxide. Is there no iron silicate in the metal?

A. L. FEILD.—I mention in a footnote that if the metal is analyzed for FeO by the ordinary method, the FeO present as iron silicate is obtained. None of the latter, however, can have been in solution in the metal. Hence it has no appreciable effect on eliminating carbon.

In addition to what Dr. Herty has said about the use of equation 7, the employment of graphs or tables holds forth interesting possibilities, since by their use the equation could be dispensed with so far as the operator is concerned.

L. F. REINARTZ.—If you used the table you would have difficulty interpreting it, would you not?

A. B. KINZEL, New York, N. Y.—I appreciate the difficulties in the application of the equation in question and I think Mr. Feild agrees with me that the time for its application is not ripe.

To put a process such as the open hearth on a scientific basis, one must proceed slowly. The first step is to discover the mechanism of the reaction. I have seen

a great many equations that attempted to state how these reactions took place, and their rates under various conditions. I have not seen one yet, until this equation 7, that has, to my mind, expressed the true state of affairs. Equation 7 states the existing conditions, and I think it is going to be classical. Mr. Feild is to be congratulated in having done a fine piece of work in setting it up.

The next step is to reduce the equation to a simple, usable form. The constants in the equation as well as the constants of the rate of reaction are probably functions of temperature. Therefore it has become increasingly important for open-hearth men to know the temperature of the metal. Knowing the temperature of the slag we are still a long way from knowing the temperature of the metal. There are several methods for determining this temperature. The one which I have communicated to Feild is the old method using a calorimeter. This all boils down to a question of materials available.

If a small tube a foot long containing a small ball of platinum is held in the metal and then extracted from the furnace and the ball placed in a mercury calorimeter, it should have all the elements of a successful measuring outfit. Whether the difficulties of carrying this out will be too great or not remains to be seen but at least I should like to suggest the very decided attractiveness of going back to what was probably one of the first methods of measuring temperature accurately.

G. B. WATERHOUSE, Cambridge, Mass.—In open-hearth work carbon has been relied upon as one of the strongest deoxidizing agents. I can hardly see what this reaction is, $C + FeO$ being slower than the rate of diffusion of FeO from the slag into the bath.

The author seems to believe that the more rapid the reaction, $C + FeO$ in the bath, the more rapid is the diffusion and of course this follows almost naturally, but it was my impression that the rate of diffusion was greater through the film and through the free surface than the reaction in the bath itself. I can hardly conceive of that happening.

A. L. FEILD.—Dr. Waterhouse has brought up the question of relative rates of diffusion and reaction. It will probably be agreed that the iron oxide originates in slag and that the FeO cannot react faster in the metal than it diffuses from the slag, otherwise in a fraction of a minute all of the available iron oxide dissolved in the metal would disappear. Rate of diffusion is usually just about equal to rate of reaction. However, the equations derived are general enough to be applicable to any possible case.

It was pointed out in the paper that, according to the equation, it is theoretically possible for the iron oxide in the metal to decrease during refining. In that case, rate of reaction would be faster than rate of diffusion while such decrease occurs. If I drop billiard balls through the roof and do not remove them as fast as they come in, the room will fill up, but I cannot, except for a limited time, take out any more than I put in. The rate of diffusion is equal algebraically to the rate of reaction plus the rate of change in the iron oxide content of the steel. If the FeO is decreasing, rate of change is negative.

L. F. REINARTZ.—You are discussing the straight slag-metal reaction without the addition of any iron ore or other addition?

A. L. FEILD.—The addition of ore does not complicate the matter unless the equation is applied to a period of operation when the ore is present in lumps or undisseminated form.

C. H. HERTY, JR.—I think Dr. Waterhouse's point was to take the billiard balls out of the room as fast as they were dropped in from the roof. That is my belief. One superintendent expressed it by saying he would like to get his heat where he

has the thirsty carbon. That simply means dragging the billiard balls out as fast as they come in and leaving a few stored in the corner to take care of that other factor.

A. L. FEILD.—The total amount of iron oxide used in the refining reactions is relatively very great. Anyone who has calculated it knows that. The total amount of FeO present at any one time in the steel is relatively very small. Yet there is actually an increase in the FeO content of the steel as the carbon drops, and to this extent the rate of diffusion is faster than rate of reaction.

C. D. KING, New York, N. Y.—Taking that as your own variable, the rate of carbon drop is in direct proportion to the area, and inversely proportional to the weight of the charge.

Those two features together mean inverse proportion to the average depth of the metal bath, which in turn means deep baths require more iron oxide. It also means deep furnaces could run with higher iron oxide in the slag without overoxidizing the metal any more than a shallow furnace with a low iron oxide in the slag. Big furnaces are in effect safer to work with so far as overoxidation is concerned.

L. F. REINARTZ.—It is, I believe, the German practice to drop the carbons more rapidly than we do because they usually have shallow baths.

H. D. HIBBARD, Plainfield, N. J.—I do not understand what Mr. Feild means by equilibrium. Does he contend that there is a point of equilibrium between carbon and oxide of iron and when that is reached there would be no boil, that is unless the metal is heavily charged with silicon or aluminum or some other gas solvent? If there is any carbon present, there is boiling going on and in that case no equilibrium in the usual meaning of the word.

A. L. FEILD.—I do not think that is so. The equilibrium constant we are speaking of is a constant or numerical ratio which has no visible physical existence. The equilibrium to which we refer exists all through the carbon drop. During the most violent boil, there exists a constant relationship as well as at the time of attainment of the final equilibrium between slag and metal. You cannot carry the carbon down to zero, commercially at least. The conditions on which the equations are based are those of ordinary practice.

C. H. HERTY, JR.—Mr. Hibbard knows, of course, that a heat can be melted dead at 0.10 per cent. or 0.127 per cent. carbon, proving the heat is cold enough. Under those conditions, there is equilibrium between carbon and oxide so that the CO is reacting with iron just as fast as carbon is.

H. D. HIBBARD.—I have never seen such a heat.

H. STYRI, Philadelphia, Pa.—It is possible to keep the concentration of iron oxide in the slag constant for a long time. In certain heats the rate of taking carbon out of the bath appeared to have the form of a unimolecular reaction indicated by $\log C$ concentrations being proportional to time.¹⁰ That would indicate that the concentration of FeO in the bath also is constant.

J. M. GAINES, JR., Pittsburgh, Pa.—The point was brought out, I think, in a general equation that either diffusion or rate of reaction is going to control the rate of carbon elimination.

L. F. REINARTZ.—What effect does rusty scrap have on this reaction?

C. H. HERTY, JR.—It would have no effect. I do not think you overoxidize the metal. You overoxidize the metal after you deoxidize it.

¹⁰ H. Styri: Theory and Practice of Steel Refining. *Jnl. Iron and Steel Inst.* (1923) 108, 216.

L. F. REINARTZ.—Suppose the charge has rusty scrap in it?

C. H. HERTY, JR.—It means faster diffusion, necessarily. More oxidizer is being introduced than is ordinarily the case.

L. F. REINARTZ.—Whenever low-silicon pig iron is used, the carbon drop is also extremely rapid.

C. H. HERTY, JR.—There is not enough silicon to deoxidize the slag and a greater amount of FeO is available for carbon elimination than in heats with high-silicon iron.

A. B. KINZEL.—Equation 7 answers the problem very nicely. In Dr. Styri's question on integration, that equation comes out in a series. The first term is the original carbon drop; the second term is the rate of carbon drop times the constant. That constant does not involve the iron oxide in the slag. For straight-line conditions, the amount of iron oxide in the slag does not have an appreciable effect. The instant that diffusion comes into play, the third term is introduced and the equation is modified and depicts conditions as they actually exist.

H. STYRI (written discussion).—It is interesting to see that Mr. Feild now admits that the calculations he presented for the Faraday Society in 1925 were inaccurate. That has already been shown in detail by Piérard.¹¹ The latter maintains, as is well known and quite evident, that where a number of interdependent reactions occur simultaneously it must be the slowest of the reactions that will decide the actual rate of forming the final product or in the present case the rate of carbon elimination. It is perfectly clear that the oxygen used for carbon elimination and the small amount of oxygen which will be needed to increase the concentration of oxygen in the steel bath must be supplied from oxygen diffused from the slag. Piérard consequently wrote the formula for this reaction $dy - pdx = \alpha dt$ corresponding to Feild's, but Piérard used α to designate that the conditions for oxygen diffusion to the steel bath were constant. It is, of course, often true that both temperature and concentration of iron oxide in the slag are constant over a considerable time. Piérard's formula is essentially the same as Mr. Feild's formula No. 3, the only exception being that Feild has introduced a coefficient of diffusion, the concentration of iron oxide in the slag and bath, as well as contact area and weight. If w stands for the concentration of "free" FeO in the slag and r for the partition coefficient between free FeO in steel and slag, this formula No. 3 is evidently correct and universal for acid and basic open hearth as well as converters. No more oxygen can be used up in a bath for carbon elimination and building up of oxygen than is introduced into the bath. But if w stands for total FeO in the slag, as indicated by Feild, the formula will serve only a limited purpose.

Feild introduces in this formula an expression for the velocity of the reaction in the bath in order to substitute the unknown quantities y and dy and uses for this the expression $\frac{dx}{dt} = kxy - m$. He evidently considers the conditions in the bath to be such that there is a noticeably larger amount of oxygen in solution than corresponding to the equilibrium and later, in fact, calculates such excess amount of oxygen. By doing this he obtains a differential formula which is insoluble and invalid, because the derivatives in the two formulas can only be identical for specific values of x , y and t and not general or arbitrary. Further, conditions for identity are unknown and may even be impossible.

If we study the different reactions that are occurring in the metal it seems perfectly reasonable to assume that all reactions in the metal on account of the very high temperatures must be extremely rapid, and this would include both the reaction

¹¹ P. Piérard: *Rev. de Mét.* (1927) 24, 47.

between the elements carbon and manganese and silicon, etc., with oxygen and the diffusion of these elements in the metal. The product of the concentration $C_{Mn} \times C_o$ or $C_c \times C_o$, etc., can therefore not be considered to exceed the solubility products to any noticeable extent. It may very well be, however, that the concentration of Mn is so low, due to early oxidation at lower temperatures during the melting down, that the solubility product $C_{Mn} \times C_o$ is less than corresponding to equilibrium while $C_c \times C_o = m$, or is in equilibrium, as, for instance, is recorded in the paper mentioned previously.¹² If the individual concentration for one reason or another is slightly disturbed, the equilibrium will rapidly be reestablished and the change in concentration, for instance of carbon, must therefore be entirely dependent on the outside source of the disturbance, such as diffusion of oxygen into the steel. In the steel bath, therefore, contrary to Feild's present opinion, it should be permissible to assume instantaneous equilibrium between the elements and for carbon and oxygen this would mean, with Feild's notations, that $xy = m$. From this would follow that $dy = -\frac{mdx}{x^2}$.

We can perhaps get a clearer picture of the process in an open-hearth furnace where carbon is oxidized, by trying to imagine the steps in the reactions:

Oxygen atoms will diffuse in a steady stream from the slag into the upper zone of the molten steel, where they will meet with carbon atoms which have diffused from the lower levels. The carbon and oxygen atoms will combine to CO and be eliminated from the bath as a gas. With the rapid diffusion of carbon in the steel it is rather evident that the concentration of oxygen will be high only in the upper part of the steel bath and that the principal reaction between carbon and oxygen will take place here. In the lower parts and main body of the bath the amount of oxygen present can hardly be noticeably higher than corresponding to the instantaneous equilibrium between the average carbon and oxygen. The consequences of this should be that the steel bath only gradually gets a higher concentration of oxygen as the carbon is eliminated.

It seems that we do not commit great error by assuming the respective concentrations of carbon and oxygen in the steel to be in equilibrium, and, providing we have the favorable condition stated by Feild of lively action in the slag so that there is no stratification, the rate of diffusion from the slag should be proportional to the excess free FeO in the slag. The condition at no boiling does not need to be considered in ordinary steel refining, while it is of great importance otherwise. The following formula should, therefore, express the rate of reaction

$$-6pdx - \frac{mdx}{x^2} = \frac{CA}{M} \left(w - \frac{m}{xr} \right) dt.$$

This equation can readily be integrated, but the writer believes that even in that form it is unnecessarily complicated and that a much simpler expression will be entirely satisfactory for a great many normal heats. It has already been stated that the variation in oxygen content of the steel cannot be great compared with the amount of oxygen used for carbon elimination. In other words, the quantity represented by $\frac{mdx}{x^2}$ is small compared with $6pdx$. It is, further, quite plain that the concentration of free iron oxide in the slag is maintained uniform for considerable time so that in the expression $w - \frac{m}{xr}$, w can be considered constant, and $\frac{m}{xr}$, at least for higher carbon contents, small relative to w . The simpler form will therefore be

$$-6pdx = \frac{CA}{M} wdt.$$

¹² H. Styri: *Op. cit.*, 194.

This formula integrated represents, of course, a straight line, meaning that the rate of elimination of the sum of the elements will be constant. If the finishing part of a heat is considered when the elements silicon, manganese and phosphorus have already been eliminated, the formula applies practically only to the carbon and the rate of elimination of the carbon should therefore be constant. The writer is convinced from a number of carefully analyzed heats that such is the case, as also reported by Feild. A graphic representation of a heat will definitely show carbon drop proportional to the time when other conditions are constant such as temperature and concentration of FeO in the slag. The graph shown in the *Journal of the Iron and Steel Institute*¹³ gives one example.

It is admittedly alluring to use the formula for reaction velocity in order to calculate the rate of carbon elimination in the bath. In the discussion on the floor, the writer referred to the condition of the bath when the iron oxide concentration in the slag and temperature were constant, under which assumption the formula for the rate of carbon elimination would correspond to that of a unimolecular reaction, or in other words, be proportional to the carbon content of the bath. Similarly, de Loisy¹⁴ made calculations for a number of different heats which gave the same result. However, de Loisy could not explain why the rates of reactions in similar systems were different for practically the same temperatures and therefore arrived at the conclusion that it was the rate of diffusion for carbon in the steel which controlled the rate of elimination because that would also lead to the same type formula. But, there are a number of objections to this argument; for instance, that the rate of carbon diffusion in the bath must be extremely rapid, and that it leads to de Loisy's conclusion that the rate of carbon elimination would be inversely proportional to the square of the depth of the metal for the same volume, which is improbable. It seems, therefore, that the simple formula which expresses the rate of carbon elimination to be proportional to the free iron oxide in the slag for a given temperature, at least in the greatest number of cases, will be entirely satisfactory for calculation of the carbon drop. Should greater accuracy be wanted, the more complete formula above could be used.

It is usually of great help to have as simple an expression as possible for reactions and the simplest formula showing the carbon to be eliminated in proportion to the diffusion of oxygen into the bath is adequate to explain a number of observations that can be made during the refining of steel.

P. Piérard, Paris, France (written discussion).—I have read with great interest Mt. Feild's study on the rate of carbon elimination, etc. From the point of view of the laws of physical chemistry, the calculations which he has carried out for the general equation 7 are quite correct. The hypotheses on which these calculations are based have been exactly indicated; these hypotheses are reasonable and receive my entire approval. It is evidently possible that the laws in question do not apply completely in the entire concentration range and in the cases where the osmotic pressure has no physical reality, but they constitute the only conducting thread which can guide us in the difficult study of the chemistry of refining. I consider the author's work as fundamental, in the existing state of our knowledge.

It is unfortunate that the operation studied by Keats and Herty did not give the author satisfactory values for the kinetic constant and the diffusion constant. In my opinion, under the circumstances the graphical method for the determination of the derivatives $\frac{dx}{dt}$, $p \frac{dx_1}{dt}$, and $\frac{d^2x}{dt^2}$ is preferable to that consisting in deriving the

¹³ H. Styri: *Op. cit.*

¹⁴ E. de Loisy: Sur la vitesse d'élimination du carbone au four Martin. *Rev. de Mét.* (1926) **23**, 369.

equation of the curve, which, by its nature, should not have a simple equation; it seems to me in every case less subject to systematic errors. It would seem desirable that a large number of heats be studied, some on the same furnace and under similar conditions, others under very different conditions, in order to see if equation 7 will give for k and C similar or discordant values. It is impossible to foresee the influence which the errors of sampling and of analysis of the samples have on the values of k and C . Another source of error is the uncertainty in regard to the constants m and r and in regard to the temperature. Hence, an extensive experimental investigation will be necessary to establish the validity of equation 7; that is to say, the accuracy of the hypotheses on which it is founded. I certainly hope that the author will be able to do this successfully.

Concerning the values of m and r given by Herty, it is very difficult to express an opinion, because it is not certain that the oxygen found in a sample taken in the course of a refining operation really represents the oxygen dissolved as FeO in the liquid metal. It so happens that at the end of the basic bessemer operation, at an average temperature of 1600° C. and in the presence of a slag containing 13 per cent. FeO, the determination of oxygen in the metal by hydrogen reduction gives values of the order of 0.4 per cent. FeO (the determinations of which I speak have been made in large number, by Chaudron; the results have not been published). The distribution constant, in this case where it is very probable that partition equilibrium is attained on account of the stirring of the metal and slag by the blast, would be about 0.03, instead of 0.01. However, it is necessary to observe that this value of 0.03 would not correspond to the solubility of FeO in iron given by Rosenhain and Tritton unless this solubility increased very rapidly with temperature. I should reserve my opinion likewise because of the possible presence of inclusions of slag (basic slag, in which the oxides are free and hence reducible by hydrogen) in the samples analyzed. I think that the most exact information on the constants m and r will result from the complete study of the system Fe-O above 1500° C. and by the transposition, by means of the law of mass-action, of the equation of equilibrium for the solid-gas phases to the liquid-gas phases in the system C-Fe-O.

The ratio $\frac{m}{r}$ is equal to the product of per cent. carbon in the metal and per cent. FeO in the slag. At 1600° C., according to Herty, this ratio would be equal to 2; a bath in equilibrium with a slag of 13 per cent. FeO would contain 0.15 per cent. carbon. Actually, at the end of the basic bessemer operation, not more than about 0.03 per cent. carbon (analysis by combustion) is found. However, the fact must not be lost sight of that the escaping gases are composed nearly exclusively of nitrogen, so that the CO pressure ought to be extremely low. If the value 0.010 is assigned m at 1600° C., the carbon at equilibrium with a slag of 13 per cent. FeO would be 0.06 per cent.; I fear that there is not here a difference between this value and the one found (0.03 per cent.) in the overblown Thomas metal, which is in agreement with the low pressure of CO. I feel that I should point out this objection to the author.

A particularly interesting point in Mr. Feild's work is the one where he evaluates, from the values of m and of k , the relative increase in oxidation of the bath resulting from the rate of carbon elimination. If the product mk actually has the value which he attributes to it, there would be here a remarkable explanation of the effect of the rate of refining on the quality of the metal—an effect well known to operating men.

However, I have difficulty in believing that a bath with 0.268 per cent. carbon would have the ability to contain 3.35 times the content of FeO, which would be in equilibrium with the carbon. Returning to the example of the basic converter, I would point out to the author that in small converters of rapid rate of operation the carbon drops from 3 per cent. in a few minutes—let us say 6 min.—so that $-\frac{dx_1}{dt}$

has a value of 0.5. Since m and k ought to be universal constants, the excess of FeO would be $\frac{0.5}{0.0102 \times 0.139} = 350$. I might well wish that elimination of carbon proceeded in the converter at a temperature below 1580° C. and that from this fact the constant m increased, but in compensation, k ought to be smaller. In fact, *at whatever moment of operation the converter is tilted down, boiling of the charge such as to lead to the supposition that the content of FeO is very different from that which would be found in equilibrium with carbon is never observed.* This objection is worthy of the author's serious consideration. The converter is the refining apparatus which best permits the realization of partition equilibrium between slag and metal; and at any time the converter is lowered the charge is practically withdrawn from every external influence. The fact that it is quiet and that no variation in composition of the metal is noticed in repose has always led me to think of the reactions as almost instantaneous.

Another objection is drawn from phenomena which accompany recarburization in the vessel. Consider a bath with 0.1 per cent. carbon and 0.25 per cent. FeO at equilibrium ($m = 0.025$, temperature = 1600° C.). Let it be recarburized to 0.5 per cent. carbon. The reaction of deoxidation, that is to say of elimination of FeO by carbon up to the equilibrium point, will be governed by equation 4:

$$-\frac{dx_1}{dt} = 0.139 (xy - 0.025).$$

It is possible to solve this, taking account of the fact that

$$0.25 - y = 6 (0.5 - x).$$

Simply let the initial rate of elimination of C be evaluated; then,

$$\begin{aligned} -\frac{dx_1}{dt} &= 0.139 (0.125 - 0.025) \\ &= 0.0139 \text{ per cent. carbon per minute.} \\ -\frac{dy}{dt} &= 0.08 \text{ per cent. FeO per minute.} \end{aligned}$$

Actually, on the other hand, the reaction does not require several minutes; it is almost instantaneous and the evolution of CO, which is a measure of it and which is easily visible, ceases very rapidly. It is probable then that k is of a much higher order of magnitude.

A. L. FEILD (written discussion).—In a private communication sent to the author prior to the presentation of the present paper, A. B. Kinzel, of the Union Carbide and Carbon Research Laboratories, proposed as an approximate solution of equation 7 a power series equation of the type

$$x = R_o + R_1(t - t_o) + R_2(t - t_o)^2 + R_3(t - t_o)^3 + \dots + R_n(t - t_o)^n \quad [13]$$

where $R_o = x_o$, $R_1 = \left(\frac{dx}{dt}\right)_o$, $R_2 = \frac{1}{2} \left(\frac{d^2x}{dt^2}\right)_o$, $R_3 = \frac{1}{3} \left(\frac{d^3x}{dt^3}\right)_o$, and, in general, $R_n = \frac{1}{n} \left(\frac{d^n x}{dt^n}\right)_o$, and the values x_o , $\left(\frac{dx}{dt}\right)_o$, $\left(\frac{d^2x}{dt^2}\right)_o$, etc., refer to a selected time t_o , which could be taken as zero when convenient. Mr. Kinzel suggests that, since the above power series is known to converge rapidly, terms beyond the third term of the right-hand member of equation 13 can be neglected for purposes of practical application. The resulting power-series equation of finite number of terms, which would represent such an approximate relationship, is the following:

$$x = x_o + \left(\frac{dx}{dt}\right)_o (t - t_o) + \left(\frac{d^2x}{dt^2}\right)_o \frac{(t - t_o)^2}{2} \quad [13a]$$

According to equation 13a, it should be possible, theoretically, to calculate the time ($t - t_0$) required for the carbon to drop from any known or selected initial value x_0 to any lower value x , provided that the values of $(\frac{dx}{dt})_0$ and $(\frac{d^2x}{dt^2})_0$ are known. Mr. Kinzel further proposes to determine $(\frac{dx}{dt})_0$ experimentally and to calculate $(\frac{d^2x}{dt^2})_0$ by means of equation (4).

The practicability of employing this mode of solution for equation 7 will be investigated and the results reported in a subsequent paper.¹⁵

Mr. Styri's reference to my Faraday Society paper¹⁶ of June, 1925, which was reprinted in the *Revue de Métallurgie*¹⁷ in 1927 and reviewed there at length by Mr. Piérard¹⁸ is both timely and pertinent. However, I feel that Mr. Styri has failed to make clear the substance of Mr. Piérard's intelligent and able review. To discuss adequately the very interesting and original features of this review, which involved higher mathematics to a considerable extent, would be impossible in the space available here. It may be stated, however, that its contents did not anticipate in any way the method of treatment and the solution which are offered in the present paper. While pointing out the fact that my former idea of "instantaneous" equilibrium involved an approximation, Mr. Piérard made use of this approximation in the main part of his mathematical treatment. The solutions offered by him for the carbon-time relationship for several assumed sets of conditions contained y or functions of y , and none of these sets of conditions was of as general a nature as that to which equation 7 is applicable. Mr. Piérard also pointed out, in effect, the fact that in equation A the coefficient w could not be considered as a part of the diffusion term proper and also that the diffusion coefficient C should depend upon slag viscosity. These two points have been discussed in the text of the present paper. The latter was referred to by Dr. C. H. Herty, Jr., in his written discussion of the Faraday Society paper; the former point was further brought to my attention independently by Dr. Herty and Mr. Kinzel in private communications received in the spring of 1927. It should be added here that it was never my idea to consider equilibrium in the metal as attainable instantaneously. In fact, I took pains to state that the attainment of this equilibrium was "practically" instantaneous.

I have carefully read the arguments which Mr. Styri advances in his discussion without being able to understand just how they are pertinent to the mathematical treatment of the present paper or to the mechanism of the process as outlined therein. I feel quite safe in saying that Mr. Piérard does not contend that the law of mass action, expressed in the form of an equation, represents an original contribution on his part, nor have I attempted to do so in this paper or in the previous paper. The mathematical treatment of the present paper is not based exclusively on the law of mass action nor, in fact, could it have been developed from this law alone. The similarity between my treatment and that of Mr. Piérard in his review, to which Mr. Styri refers, is not significant.

The discussion of the present paper, which Mr. Piérard has submitted in a written communication, shows a clear grasp of the principles involved and raises a number of interesting and important questions. If the mechanism of the oxidation process in the basic converter is substantially identical with that which prevails in the basic open hearth, it would be difficult—if not impossible—to obtain a satisfactory answer

¹⁵ See A. L. Feild: The Equation of the Carbon-time Curve in Basic Open-hearth Refining and Prediction of Carbon Drop. Amer. Soc. Steel Tr. (1928).

¹⁶ The date of this paper is erroneously given in *Revue de Métallurgie* as June, 1926.

¹⁷ *Rev. de Mét.* (1927) 24, 41.

¹⁸ *Idem*, 47.

to some of these questions. While I must plead lack of actual experience with basic converter practice, it appears to me probable that oxidation of carbon in the basic converter is brought about not entirely by diffusion of iron oxide from the slag but by a direct contact of the oxidizing blast with the molten metal. In the latter case, the percentage of FeO dissolved in the metal during the blow would be greater than that predicted on the assumption that slag-metal equilibrium obtained. During the blow and for a period subsequent thereto, diffusion of FeO would be outward from metal to slag. Mr. Piérard's observations on the phenomena which accompany recarburization in the vessel present a somewhat more difficult problem. It is conceivable, however, that the decrease in the percentage of dissolved iron oxide brought about by recarburization corresponds to a volume of CO which is hardly more than sufficient to saturate the metal with CO and that it is only the excess CO which escapes. This suggestion presupposes, of course, that the metal is not saturated with CO at the conclusion of the blow, due to the partial pressure of nitrogen. I agree with Mr. Piérard that the value of k as calculated in the present paper appears to be low. More satisfactory and more extensive open-hearth data should enable the value of k to be calculated with considerable accuracy. At the same time, whether or not equation 7 is of general applicability to the basic open hearth could be proved conclusively.

Effect of Temperature on the Solubility of Iron Oxide in Iron*

By C. H. HERTY, JR.† AND J. M. GAINES, JR.,‡ PITTSBURGH, PA.

(New York Meeting, February, 1928)

IRON oxide (FeO) plays an extremely important part in the manufacture of steel. In the open-hearth furnace and the Bessemer converter it is the chemically predominant compound and controls to a large extent both the operation of the furnaces and the composition and quality of their products. Almost all of the refining action is carried out through the medium of FeO , which oxidizes carbon, manganese, silicon and phosphorus.

At the end of any open-hearth or Bessemer heat the steel contains dissolved iron oxide, which must be wholly or partly eliminated. The type of deoxidation product depends on the amount of dissolved iron oxide and on the deoxidizer used. After the heat has been deoxidized and while it is being teemed, iron oxide diffuses from the ladle slag into the metal, causing losses of deoxidizer and increase in iron oxide content of the steel.

It is generally believed that non-metallic inclusions are responsible for a great many failures of steel in service and for decreased yield of steel during rolling. The basis of most non-metallic inclusions is dissolved iron oxide.

This investigation was undertaken in order to determine the amount of iron oxide that will dissolve in iron under various conditions. Steel-making slags are complex and it has been thought best to determine solubility under simple slags as a first step. The study is being continued under slags whose compositions approach those of operating slags.

PREVIOUS INVESTIGATIONS

The solubility of oxygen in iron has been determined by a number of investigators (see Table 1) but their efforts have been directed toward the

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A discussion of some phases of the results and experimental procedure, and some preliminary tests of the physical properties of the iron-oxygen alloys made in this work may be found in *Bull. 34, Mining and Metallurgical Investigations, Carnegie Institute of Technology, 1927.*

† Physical Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

‡ Assistant Physical Chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines.

solubility at the melting point of iron, 1535° C. In the determination reported by the Bureau of Standards, a number of values for oxygen in iron, ranging from 0.24 to 0.28, are given. These, however, were determined after the metal had been exposed to an oxidizing flame in addition to simple melting. It is very probable that the reason for these higher values is that the metal was considerably above its melting point. It should be noted here that de Coussergues¹ quotes Eichhoff as giving a curve

TABLE 1.—*Solubility of Oxygen in Iron at Its Melting Point*

Investigator	Oxygen, Per Cent.	Remarks	Reference
Austen.....	0.280	No temperatures given.	<i>Jnl. Iron and Steel Inst.</i> (1915) 92 , 157
U. S. Bureau of Standards.....	0.21	At melting point.	<i>Chem. & Met. Eng.</i> (1922) 26 , 778.
Tritton and Hanson.....	0.21	At melting point.	<i>Jnl. Iron and Steel Inst.</i> (1924) 109 , 90.
Herty.....	0.27	Above melting point.	<i>Trans.</i> (1926) 73 , 1107.
Herty.....	0.22	At melting point.	<i>Op. cit.</i>

for the solubility of iron oxide in iron against temperature. On referring to the original article,² however, it is found that Eichhoff assumed the solubility curve and that no determinations were made.

From the results just given it is very evident that the solubility at the melting point may be called 0.21 per cent. oxygen, inasmuch as all investigators agree on this point. Unfortunately, none of the higher values have corresponding temperature figures, so they must be thrown out as far as quantitative discussion is concerned.

EXPERIMENTAL METHOD

In making determinations on the solubility of iron oxide in iron, a 50-kw. Ajax-Northrup furnace was used. This was equipped with a magnesia-lined graphite crucible in which 50 lb. of electrolytic iron was melted and held at the required temperature. When the metal was melted, the desired slag—either iron oxide or a mixture of lime and iron oxide—was added in sufficient quantity to give a liquid ring on the surface of the metal. Temperature readings were taken at frequent intervals and when the temperature had been constant for 15 min., samples of slag and metal were taken. The slag was analyzed by the usual laboratory methods for FeO, Fe₂O₃, SiO₂, MgO, and CaO. One or two samples of metal from each heat were analyzed for the usual constituents, carbon,

¹ C. de Coussergues: Influence of Temperature in the Manufacture of Steel. *Rev. de Met. Mem.* (1922) **19**, 641.

² Eichhoff: Advance in Electric Steel. *Stahl und Eisen* (1907) **27**, 48.

manganese, phosphorus, etc., and all samples were run by the modified Ledebur method for ferrous oxide content.

From the slag analysis the mol per cent. of FeO in the slag was calculated. This value, together with the determined quantity of FeO in the metal in equilibrium with this slag, enabled calculation of the distribution of iron oxide between slag and metal by the ratio

$$\frac{\text{mol per cent. FeO in the slag}}{\text{per cent. FeO in the metal}}$$

From the distribution ratio a value for the solubility under a slag of 100 mol per cent. FeO was determined, and this value plotted against observed temperature was used in preparing the solubility curve.

Sampling

Samples of metal from the melt were taken with a steel spoon. An attempt was made to coat this spoon with magnesia, but it was found that the sudden heating caused the magnesia to crack off almost at once. For this reason, fireclay coating was used on the spoon, even though a small amount of silica was introduced into the slag thereby.

The action of the current in the furnace causes a violent boil of the metal, which results in very intimate contact at the slag-metal surface and throws slag into a ring around the top of the metal surface. On account of this, the question arose as to whether or not any slag was entrapped in the metal during the boiling. In order to determine whether or not this was so, samples were taken with power on, then the power was shut off and another sample was taken 1.5 min. later. These showed no appreciable difference in FeO content, indicating that the samples with the power on did not contain entrapped slag (see Table 2). This conclusion was verified by making an analysis for lime in metal samples taken under lime-iron oxide slags. No traces of lime could be detected in these samples. It will be noted that very close checks were obtained between all samples except No. 9 and 10, and this discrepancy is probably due to other causes.

TABLE 2.—Effect of Boiling of Metal on Slag Inclusion

Sample No.	FeO, Per Cent. Boiling	Sample No.	FeO, Per Cent. Quiet
7	1.01	8	1.01
9	1.42	10	1.07
11	0.93	12	0.93
13	0.88	14	0.83
15	1.01	16	1.04
17	0.98	18	0.99
19	0.89	20	0.89
21	1.21	22	1.17

In the first heat, metal samples were poured into an ordinary test mold such as is used in open-hearth shops. After the first two or three samples, when the metal became fairly high in FeO, it was apparent that some of the iron oxide was coming to the surface on account of the slow cooling of the relatively large mass of sample. For the last two samples on this heat (No. B) the mold was cooled with water, which effectively entrapped all of the dissolved iron oxide. On subsequent heats a special mold was used, consisting of a thin wedge cut in a rather large block of steel. This provided a heat reservoir which chilled the metal almost instantaneously and insured very good sampling conditions. Samples of slag were taken by shutting off the power momentarily and dipping a cold spoon into the surface of the slag. The slag chilled on the spoon and was then knocked off and preserved for analysis.

Measurement of Temperature

The temperature of the metal in all heats was measured with a Leeds and Northrup optical pyrometer. Because the metal in the crucible was neither under black-body conditions nor free-radiating, a correction for emissivity had to be determined and applied. This was done by using a bath of pig iron in which a silica tube protected by a graphite casing could be immersed. Temperatures were read both on the free surface and on the bottom of the closed tube and the differences noted. Table 3 shows the comparison between the true temperature and the observed temperature, obtained by sighting on the metal surface.

TABLE 3.—*True Temperature Measurements*

Observed Temperature ⁽¹⁾	True Temperature ⁽²⁾	Ratio (2, 1)
1300	1394	1.072
1350	1449	1.072
1400	1504	1.073
1450	1566	1.080
1500	1630	1.087
1550	1697	1.093

All the temperatures recorded in the experimental heats were corrected by these data, except heat EE, in which advantage was taken of the fact that the slag formed an overhanging ring above the metal surface and it was possible to sight underneath this ring where conditions closely approximating black-body conditions prevailed. With the metal just at the melting point on the occasions mentioned, the correction was found to be 1.01 and this factor was used in determining true temperatures on heat EE.

EXPLANATION OF UNITS USED

Mol Per Cent. FeO in the Slag.—In determining the activity of a substance in solution it is necessary to know its concentration in terms of molecules instead of weight units. The molecular per cent. of a substance in solution is the number of molecules of the substance divided by the total number of molecules present, and is commonly termed "mol per cent." The relative number of molecules of two or more substances in solution is obtained by dividing the weight per cent. of each by its molecular weight. The mol per cent. of any one is then easily determined. For example: consider a slag analyzing 50 per cent. FeO, 40 per cent. CaO, and 10 per cent. MgO: The relative molecular concentrations are:

$$\text{FeO} = \frac{50}{71.85} = 0.696$$

$$\text{CaO} = \frac{40}{56.0} = 0.715$$

$$\text{MgO} = \frac{10}{40.3} = 0.248$$

The total mols are equal to the sum of the three = $0.696 + 0.715 + 0.248 = 1.659$ and the "mol percentages" are:

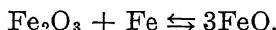
$$\text{FeO} = \frac{0.696}{1.659} = 42.0 \text{ per cent.}$$

$$\text{CaO} = \frac{0.715}{1.659} = 43.1 \text{ per cent.}$$

$$\text{MgO} = \frac{0.248}{1.659} = 14.9 \text{ per cent.}$$

If definite compounds of two or more substances exist in the liquid slag they must be taken into account as compounds and not as mixed oxides in calculating mol per cent. of any component of the slag.

Correction for Fe₂O₃ in the Slag.—Fe₂O₃ present in the slag is considered as being reduced to FeO at the slag-metal surface by the reaction



All slags have been corrected for Fe₂O₃ by this equation.³

RESULTS

Fig. 1 shows the distribution ratio

$$\frac{\text{mol per cent. FeO in the slag}}{\text{weight per cent. FeO in the metal}}$$

plotted against temperature. Fig. 2 shows the solubility curve, obtained from Fig. 1 by the relation

$$\text{Solubility of FeO} = \frac{100}{\text{the distribution ratio}}.$$

³ C. H. Herty, Jr.: Chemical Equilibrium of Manganese, Carbon, and Phosphorus in the Basic Open-hearth Process. *Trans. (1926)* **73**, 1107.

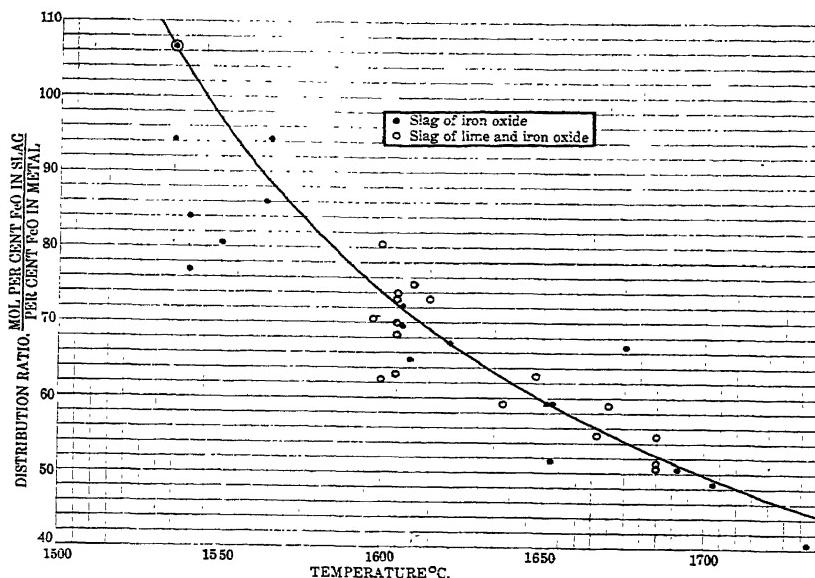


FIG. 1.—EFFECT OF TEMPERATURE ON THE DISTRIBUTION OF IRON OXIDE BETWEEN SLAG AND METAL.

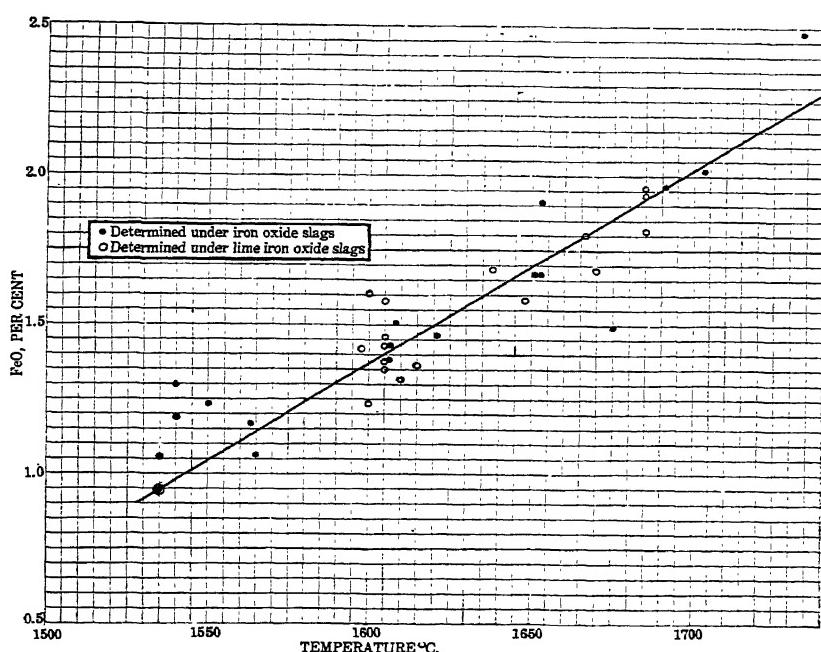


FIG. 2.—EFFECT OF TEMPERATURE ON SOLUBILITY OF FeO IN IRON.

At 1600° C., the normal open-hearth tapping temperature, the solubility of FeO in iron is 1.36 per cent. FeO (0.304 per cent. O₂). At 1700° C. the solubility increases to 2.02 per cent. FeO (0.452 per cent. O₂).

Table 4 gives the essential data on FeO on all heats made. Table 5 gives typical metal and slag analyses. In general, the magnesia crucibles held up well under the action of the slag.

DISCUSSION OF RESULTS

Solubility Curve

It will be noted that at temperatures just above the melting point the per cent. FeO in the metal is somewhat higher than the straight line given in Fig. 2. At these low temperatures it was almost impossible to effect a clean separation of slag and metal, as a large part of the sample would freeze in the sampling spoon. As the temperature was raised, a good separation was obtained and perfectly clean samples resulted. A few points at 1540° C. were so very high in iron oxide, on account of trapped slag, that they have been omitted in Fig. 2 and Table 4. The straight-line relationship between temperature and FeO content of the metal has been drawn neglecting the four determinations at temperatures just above the melting point.

Form in Which Oxygen is Dissolved in the Metal

The fact that increasing amounts of oxygen are found in the metal with increasing temperature indicates that oxygen dissolved in the metal is present as a compound and not as a gas. Gas dissolved in liquids shows decreasing solubility with increasing temperature. Knowledge of the compound formed may be obtained from a consideration of the distribution ratios given in Table 4. Nernst,⁴ from theoretical considerations and experimental evidence, formulated the law of distribution which may be summarized as follows: If a substance be dissolved in two immiscible or slightly miscible liquids (in this case slag and metal), it possesses a constant distribution coefficient at a given temperature when it exists as the same molecular species in both solvents. Table 6 gives the distribution ratios observed over the temperature range 1598° to 1615° C. The distribution ratio is constant over a wide range in mol per cent. FeO in the slag, the average per cent. deviation in distribution being 5.45 per cent. This shows that the oxygen in the metal is present as FeO.

* W. Nernst: Distribution of a Substance between Two Solvents and between Solvent and Gas. *Ztsch. f. phys. Chem.* (1891) **8**, 110.

TABLE 4.—*Results of Solubility Determinations*

Sample No.*	Temperature, ° C.	Mol Per Cent. FeO in Slag (1)	Per Cent. FeO in Metal (2)	Distribution Ratio = (1) (2) = (3)	Solubility, Per Cent. FeO
B-7.....	1734	91.8	2.28	40.2	2.48
D-9.....	1703	84.0	1.73	48.4	2.02
D-8.....	1691	88.5	1.75	50.4	1.97
BB-17, 18.....	1685	50.5	0.99	51.1	1.96
BB-19, 20.....	1685	49.0	0.89	54.8	1.82
EE-11.....	1685	56.0	1.09	51.5	1.94
D-7.....	1675	90.8	1.35	66.8	1.49
BB-9, 10.....	1670	63.3	1.07	59.4	1.68
BB-11, 12.....	1667	53.0	0.96	55.5	1.80
D-2.....	1653	99.8	1.92	51.7	1.92
D-1.....	1653	99.8	1.67	59.5	1.67
D-6.....	1652	92.4	1.54	59.5	1.67
BB-7, 8.....	1648	63.5	1.01	63.2	1.58
BB-13, 14.....	1638	51.2	0.86	59.5	1.68
E-9.....	1621	88.2	1.30	67.7	1.47
EE-10.....	1615	64.5	0.88	73.4	1.36
EE-2.....	1610	86.9	1.15	75.6	1.32
B-9.....	1609	91.8	1.39	65.1	1.51
D-4.....	1606	97.6	1.35	72.5	1.38
E-8.....	1606	89.5	1.28	69.8	1.43
EE-1.....	1605	90.9	1.25	73.0	1.37
EE-3.....	1605	84.8	1.15	73.8	1.35
EE-6.....	1605	73.5	1.16	63.4	1.58
EE-7.....	1605	73.7	1.05	70.0	1.43
EE-8.....	1605	73.4	1.08	68.3	1.46
EE-5.....	1600	77.5	1.25	62.3	1.61
EE-9.....	1600	71.3	0.89	80.5	1.24
EB-5, 6.....	1598	72.8	1.04	70.3	1.42
E-7.....	1565	96.0	1.04	94.2	1.06
E-4.....	1564	96.0	1.12	86.0	1.17
E-1.....	1550	96.0	1.19	80.6	1.24
E-2.....	1540	96.0	1.15	84.0	1.19
E-5.....	1540	96.0	1.24	77.2	1.30
BB-1.....	1535	100.0	1.06	94.2	1.06

* Single letters refer to heats with iron oxide slags; double letters to heats with lime-iron oxide slags.

TABLE 5.—*Typical Slag and Metal Analyses*
From Experimental Heats under Iron Oxide Slags

Component	B, Per Cent.	D, Per Cent.	E, Per Cent.
<i>Metal</i>			
C.....	0.007	0.011	0.009
Mn.....	None	None	
P.....	0.006	0.005	0.007
Si.....	0.007		0.003
S.....	0.019	0.016	0.011
<i>Slag</i>			
FeO.....		75.0	83.3
Fe ₂ O ₃		15.0	12.5
SiO ₂		2.20	1.70
CaO.....		None	None
MgO.....		6.80	3.2
S.....		0.074	

From Experimental Heats under Lime-iron Oxide Slags

Component	BB, Per Cent.	EE, Per Cent.		
<i>Metal</i>				
C.....	0.003	0.006		
Mn.....	None	None		
P.....	0.004			
Si.....	0.004			
S.....	0.018	0.016		
<i>Slag</i>				
	First Slag	Last Slag		
	First Slag	Last Slag		
FeO.....	58.50	33.90	76.50	38.90
Fe ₂ O ₃	18.70	21.20	14.20	21.30
CaO.....	14.85	25.15	0.74	32.80
MgO.....	7.75	20.65	4.74	6.66
SiO ₂	1.60	1.00	2.30	1.88

TABLE 6.—*Constancy of Distribution Ratio with Varying Mol Per Cent. FeO in the Slag*

Sample	Temperature, Deg. C.	Mol Per Cent. FeO	Distribution Ratio
D-4.....	1606	97.6	72.5
B-9.....	1609	91.8	65.1
EE-1.....	1605	90.9	73.0
E-8.....	1606	89.5	69.8
EE-2.....	1610	86.9	75.6
EE-3.....	1605	84.8	73.8
EE-5.....	1600	77.5	62.3
EE-7.....	1605	73.7	70.0
EE-6.....	1605	73.5	63.4
EE-8.....	1605	73.4	68.3
BB-5, 6.....	1598	72.8	70.3
EE-9.....	1600	71.3	80.5
EE-10.....	1615	64.5	73.4
Average.....	1605		70.6

Dissociation of Compound in Liquid Slags

All the slags contained considerable amounts of Fe_2O_3 , because of oxidation of the slag by the gases over the melt. The lime-iron oxide slags contained about 5 per cent. more Fe_2O_3 than the slags without lime. This was due either to the formation of calcium ferrate or to slower diffusion of Fe_2O_3 to the slag-metal surface, the lime-iron oxide slags being somewhat more viscous than the slags containing only iron oxide. The fact that the distribution ratio, $\frac{\text{mol per cent. FeO in slag}}{\text{weight per cent. FeO in the metal}}$, was the same for both iron oxide and lime-iron oxide slags at a given temperature shows that if any compound, such as calcium ferrate, was formed, it was dissociated at the slag-metal surface.

Active FeO in the Slag

The solubility curve gives the saturation value for FeO in iron under a slag of pure iron oxide. The distribution ratio curve is a quantitative statement of the relation between iron oxide in the slag and FeO in the metal and applies only to equilibrium conditions. The term "mol per cent. FeO in the slag" refers only to that portion of the FeO which is free to dissolve in the metal and, as pointed out in the preceding paragraph, in lime-iron oxide slags all of the iron oxide is in such a condition. If stable compounds of FeO and another oxide are present the amount of FeO dissolved in the metal would be less than that predicted from the mol per cent. of "total FeO" in the slag but would be proportional, by the value of the distribution ratio, to the "free" FeO content of the slag.

Solubility of FeO in Iron under Operating Slags

From the foregoing discussion it can be seen that the exact amount of FeO in the metal in equilibrium with a finishing open-hearth or Bessemer slag can not be predicted until data are obtained on the compounds present in such slags. The initial steps toward a knowledge of solubility of FeO in iron under commercial slags are determinations of solubility under slags consisting of FeO and SiO₂, and FeO, CaO and SiO₂. The distribution ratio curve, Fig. 1, may be used as a reference line for any determinations, as it gives the FeO in the metal which is in equilibrium with "free" FeO in the slag.

Furthermore, in open-hearth operation, equilibrium between slag and metal is seldom reached because carbon elimination is proceeding at all times, preventing the metal from taking up iron oxide to its equilibrium value. Under open-hearth conditions the amount of dissolved iron oxide depends on the carbon content of the metal and the temperature, unless of course, deoxidation with some other metalloid has taken place.

The rate at which carbon is eliminated is controlled primarily by the rate of diffusion of iron oxide from the slag into the metal and this to a large extent depends on the saturation value of FeO in the metal under the slag in question.

Inclusions in Pure Iron-oxygen Alloys

In polished sections, only one type of inclusion occurs, in the form of light gray rounded areas of various sizes. These are probably globules of FeO, saturated with iron. In a sample with 0.90 per cent. FeO the globules are all relatively small and comparatively uniform in size, as shown in Fig. 3a. With increasing FeO content above 0.94 per cent., a gradually increasing number of much larger inclusions is found, as shown in Fig. 3b, a melt containing 1.75 per cent. FeO. Many of these are nearly perfect spheres, but most of them have rounded projections on the side, and appear to be in the process of growth by the coalescence of two or more globules. The solubility of iron oxide in iron at the melting point is 0.94 per cent. FeO. If the iron oxide content of the iron is less than 0.94 per cent., no iron oxide is precipitated on cooling the melt until solidification occurs. The iron oxide then appears as finely divided globules throughout the mass of iron. On the other hand, if the iron oxide content of the melt is above 0.94 per cent., iron oxide is precipitated in the liquid iron until freezing occurs and the globules so precipitated coalesce very rapidly. Fig. 3c shows a sample of 2.46 per cent. FeO containing two large particles in the act of coalescing. This section was taken from the top of a slowly cooled ingot.

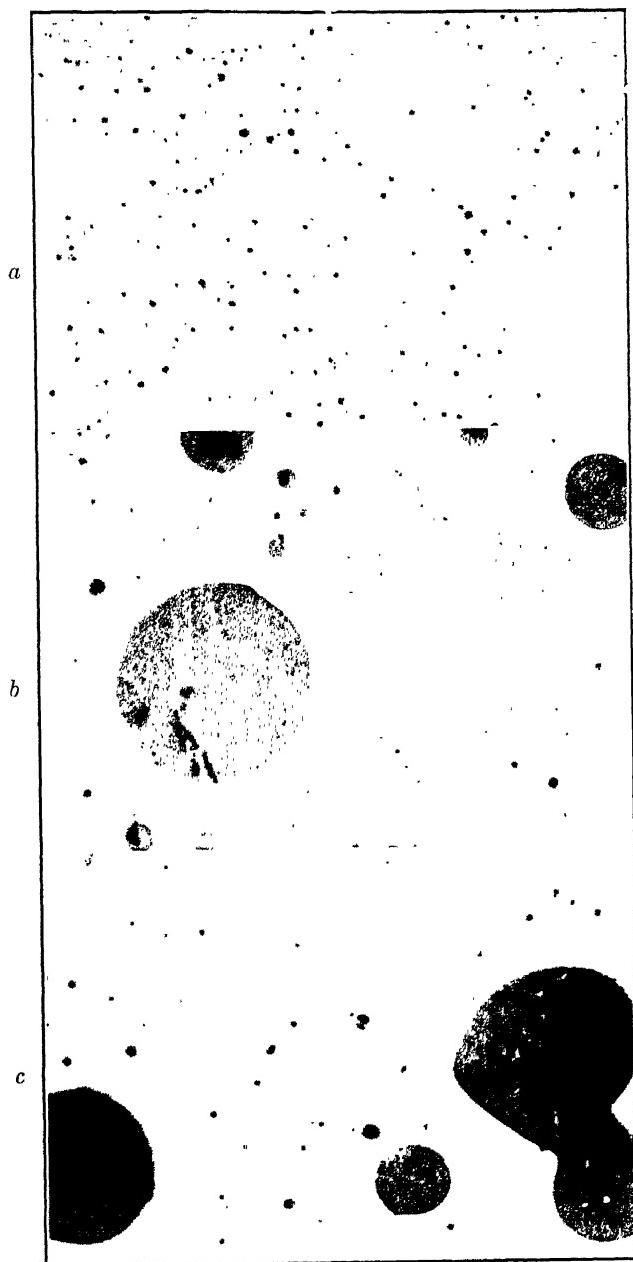


FIG. 3.—INCLUSIONS IN IRON-OXYGEN ALLOYS. $\times 250$. *a*, $\text{FeO} = 0.90$ PER CENT.; *b*, $\text{FeO} = 1.75$ PER CENT.; *c*, $\text{FeO} = 2.46$ PER CENT. (SECTION TAKEN FROM TOP OF SLOWLY COOLED INGOT, SHOWING PARTICLES IN PROCESS OF COALESCENCE.)

ACKNOWLEDGMENT

The writers wish gratefully to acknowledge the assistance rendered by W. A. Simkins, assistant analytical chemist, U. S. Bureau of Mines, who developed the apparatus and performed the analyses for oxygen. They also wish to express their appreciation to R. L. Geruso and S. P. Watkins, research fellows, Carnegie Institute of Technology, for their part in the experimental work.

DISCUSSION

J. T. MACKENZIE, Birmingham, Ala.—I have followed the development of the determination of oxygen for some time, in Germany, in England and here. Were any of these samples checked on large samples by the vacuum fusion method?

C. H. HERTY, JR.—These particular samples were not checked by the vacuum fusion method, but in running the apparatus in the last two or three years, there have been developed a number of new absorbents and gas-purifiers which enable one to make a much more accurate measure than possibly 10 years ago.

I did some solubility work at Massachusetts Institute of Technology in 1922. I had to run blanks which amounted to as much oxygen as I had in the sample, which made the determination seriously open to question. But with the apparatus we have developed with the new absorbers, we get a blank which is four zeros.

I think Cain and Pettijohn⁵ showed that a sample milled under oil absorbs no oxygen during the milling. We milled samples of killed steel under oil and got as low as 0.001 per cent. oxygen. Of course, in the samples reported in this paper one could have had a big blank on the apparatus and still been close. The amount of oxygen dissolved was so large that any experimental error was small. We held everything down to zero blank on the apparatus before we went ahead with the determination.

J. M. GAINES, JR., Pittsburgh, Pa.—In continuation of the work which Dr. Herty has just described, we have been working, during the last year, on the effect of silica in the slags on the distribution of FeO between slag and metal.

We find that iron oxide and silica exist as a partially stable silicate in liquid slags. Therefore the iron oxide in the slag is not wholly free to dissolve in the iron and the amount dissolved for a given per cent. FeO in the slag is less than would be predicted from the distribution ratio for pure iron oxide or for lime-iron oxide slags.

The compound—2FeO.SiO₂—tends to break up more completely at higher temperatures, as shown by the figures in Table 7, for a slag containing 60 per cent. FeO with either silica or lime.

TABLE 7.—*Per Cent. FeO in Metal under Lime-iron Oxide and Silica-iron Oxide Slags*

TEMPERATURE	FE _O IN METAL, PER CENT.		RATIO SiO ₂ — FE _O CaO — FE _O
	CaO — FE _O	SiO ₂ — FE _O	
1540° C.	0.53	0.25	0.47
1565° C.	0.61	0.46	0.75

Indications are that the ratio approaches unity around 1600° C. This illustrates why temperature plays such an important part in the working of the acid open hearth.

⁵ J. R. Cain and E. Pettijohn: A Critical Study of the Lebedur Method for Determining Oxygen in Iron and Steel. U. S. Bur. Stds. Tech. Paper 118 (1919).

L. F. REINARTZ, Middletown, Ohio.—This subject is of importance to the practical melter because it shows he can control his operations very closely, provided he maintains equal slag volume.

G. B. WATERHOUSE, Cambridge, Mass.—I would like to see the Bureau of Mines develop a quick method of evaluating the FeO in open-hearth slag. If this work is going to be valuable, we need a quick way of determining in the open hearth what we have in the slag. Perhaps the Bureau has done this. It would enable us to take a sample of open-hearth slag in any period in which to determine the available or probably the total FeO, and some of the other factors that we would like to have in regard to the slag.

C. H. HERTY, JR.—We are analyzing the slags for iron oxide at one or two steel plants in the Pittsburgh district. On high-carbon steels, where one has to work very close, the iron oxide is in the slag before the carbon is analyzed in the melting. The iron oxide analysis is valuable in estimating what to do. We have not been so concerned as to the lime. Most of the time the lime is in the slag anyhow and in 90 per cent. of the cases, it is unnecessary to add more.

C. B. WATERHOUSE.—I hope Dr. Herty will include the description of the quick method for FeO in his reply to the discussion. I know we shall all find it very helpful.

L. F. REINARTZ.—Have you made tests that show FeO in the slag?

C. H. HERTY, JR.—It was interesting to check up the induction furnace with the open hearth. I believe that the calcium ferrate in the slag is broken off and CO and simple slags form at the bottom surface of the slag.

L. F. REINARTZ.—Has the FeO content any relationship to the ore in the bath?

C. H. HERTY, JR.—I could not say.

L. F. REINARTZ.—If there is undigested ore in the slag does it show in the analysis?

C. H. HERTY, JR.—I do not believe it would.

L. F. REINARTZ.—Do you use this method in your accurate determination?

C. H. HERTY, JR.—What we do is to demagnetize the slag. We have never been able to spot lumps of undigested ore big enough to be sure we had undigested ore present.

A. L. FEILD, New York, N. Y.—Have you made any observations on the effect of ore additions on the iron oxide content of the slag after the ore has dissolved; that is to say, on what proportion reacts directly on the metal surface and how much goes into solution in the slag? I have seen cases where a slag, after reasonably heavy additions of ore, actually analyzed no higher in iron oxide 40 min. later.

I would like to emphasize the importance of Mr. Gaines' remarks on some of the recent work of the Bureau of Mines. The FeO in an acid slag would appear to behave at high temperatures very much like the FeO in a basic slag. While there are great differences between the acid and basic open-hearth processes, 1 per cent. of iron oxide in the acid slag is approximately equivalent to 1 per cent. in the basic slag.

C. H. HERTY, JR.—In the acid slag, a much higher temperature is necessary in order to have the two alike. Elimination of carbon probably would not begin until one was ready to tap. At ordinary temperatures one would have less free iron oxide in the slag, and the acid furnace would be hotter.

On the subject of ore addition, I think the type of ore used must be considered; it is hard to tie down to any general system. If heavy black ore is used most of it goes into the metal and less iron oxide is obtained in the slag from it than with the

red. The red ore dissolves in the slag and gives a higher iron oxide. It is also necessary to know the slag volume accurately.

L. F. REINARTZ.—What was the size of the ore? If the ore is fine it will stay in the slag. The lump ore will go down in the metal and do more good.

C. D. KING, New York, N. Y.—In iron oxide equilibrium as worked out by Dr. Herty, how would a low iron oxide content be obtained?

C. H. HERTY, JR.—The iron oxide in the slag must be kept as low as possible. This can be accomplished in three ways. First, keep down the amount of iron oxide in the slags during melting by charging the proper kind and amount of raw materials. Avoid charging excessive amounts of ore or small rusty scrap, and get the scrap under cover as quickly as possible. There are certain types of charges, of course, where all of the iron oxide used during the melting stage comes from scrap oxidation and the operator should work to get from the charge just the amount of iron oxide he requires, and no more. Second, do not use any more ore than is necessary during the working period and particularly do not use ore too close to tap. Third, during the working and finishing periods, avoid an atmosphere that is too greatly oxidizing.

C. D. KING.—Would there be any difference in the furnace operating with run-off slag as against one that has none?

C. H. HERTY, JR.—It is difficult to compare them because they charge up differently. If you have a furnace with a run-off slag and one without the run-off slag and working on the same charge, it will be found that the latter will have a higher oxide all the way through the heat.

C. D. KING.—That checks with actual practice.

L. F. REINARTZ.—The work being done on open-hearth construction will help a lot here. We think we can control the atmosphere in furnaces and have oxidizing conditions during charging and melting of the heat and then have non-oxidizing conditions at the end of the heat. If ore is added within a short time of tapping heat, there is bound to be oxidation due to it. If delayed 1 hr. or $1\frac{1}{2}$ hr. it takes longer to make the heat and costs more money but the quality of the steel is better.

J. O. HANDY, New York, N. Y.—Has the manganese any effect on it?

C. H. HERTY, JR.—Within the limits found in normal open-hearth furnace slags and metals I do not believe that MnO in the slag or manganese in the metal have any effect on the solubility of iron oxide. Oberhoffer and Schenck showed the effect of MnO when only MnO and FeO were present in the slag.

J. O. HANDY.—Have you made any determination to show the proper method when the residual manganese was higher?

C. H. HERTY, JR.—So far, the data we have do not show it. Where the theory is sound, I do not see how the residual manganese could have any effect. I could see where the amount of FeO in the metal would run the residual manganese up or down. You can have 0.10 per cent. or 0.25 per cent. residual and still have the same effect.

L. F. REINARTZ.—We have had the same experience whether the manganese oxide is low or high. Manganese oxide has a decided influence on the physical quality of the slag because the slag is much more fluid with a high-manganese oxide slag than with a lower percentage.

C. H. HERTY, JR.—The most important effect of high-manganese iron is desulfurization of the pig iron, much better working slag and high residual manganese, with a saving of ferromanganese. We are obtaining data on that at the present time.

Steel for Aircraft Construction

BY EDWARD ADAMS RICHARDSON,* BETHLEHEM, PA.

(New York Meeting, February, 1928)

AS DEVELOPED up to the end of the Great War, an airplane was essentially a mechanism of wood and fabric, joined and held together by metal fittings and fastening. The engine and accessories, wire for wheel spokes and other tension members, and the occasional use of metal for interplane struts and the shafts of surface controls required some metal, but essentially it was a wood and fabric structure. Attempts had been made to use metal for other purposes, such as struts in the drag-trussing of wing panels and for short interplane struts, and Junkers had produced an airplane of iron in 1915. By 1917 he was using steel tubes and duralumin sheets, securing noteworthy advantages aerodynamically and from the standpoint of weight and upkeep. He was a pioneer along lines in which progress is still being made.

PRINCIPLES OF AIRPLANE CONSTRUCTION

The loaded weight of airplanes ranges from 500 lb. for the light plane of which we heard so much a short time ago, to about 40,000 lb. The great majority of planes range from 2000 to 10,000 lb. Of this weight from 15 to 30 per cent. is for the dividend-earning load. This percentage is so low that every per cent. saved on the rest of the weight increases the pay load from 3 to 6 per cent. The economic value of every pound that can be saved in designing or constructing a plane is sufficiently great to warrant spending money on refined methods of structural analysis, materials of superior strength properties for a given weight, methods of manufacture which may make possible the use of refinements in structural design, and the like, to an extent unknown heretofore.

The weight of the airplane, without fuel, oil and crew, and pay load, ranges from 50 to 65 per cent. of the total weight loaded for planes suitable for commercial use. It is doubtful if the structural weight will ever be brought down to as low as 40 per cent. for commercial planes. The airplane may be roughly divided into:

(1) *Power plant*, which includes engines, radiators, cooling water, oil and fuel tanks, piping, propellers, engine-starting systems, pumps, super-

* Associate, Society of Automotive Engineers.

chargers, reducing gears, and the like, but excludes instruments, fuel and oil.

(2) *Fuselage and engine nacelles*, including the structural skeleton and enclosing cover necessary, ready for the installation of wings, tail surfaces, landing gear, power plant, and equipment. It is customary to charge any foundations, structural additions, or weight for supporting the loads, or for making the plane fit the particular traffic for which it is intended, to an account for "furnishings" as distinct from the essential structure.

(3) *Wing cells*, including the wing or wings, struts and bracing wires, together with aileron (wing flap) surfaces ready for erection on the fuselage, but not including the weight of any gear necessary for operating the ailerons.

(4) *Tail surfaces*, including in general the horizontal fixed surfaces or stabilizers, the horizontal movable surfaces or elevators, the vertical fixed surfaces or fins, and the vertical movable surface or rudder, together with the necessary bracing struts and wire, hinges, and the like, but not including any gear necessary for their movement or operation.

(5) *Landing gear*, including wheels, brakes, axles, struts, wires, and bolts ready for attaching to the fuselage; also the tail skid, its shock absorbers and attaching bolts. In a seaplane, all floats with their necessary supporting structure ready for attachment to the fuselage and wings.

(6) *Surface controls*, including the stick and rudder-bar (or equivalent mechanism) and all parts necessary for operating the control surfaces, including horns on the surfaces, cables or pull tubes, pulleys with their brackets and housings or bell cranks and their supports, and gearing for varying the setting of the horizontal stabilizer. Servo-motor devices and accessories would be included on large ships.

Power-plant instruments include tachometers, ammeters, voltmeters, oil pressure gages, fuel gages, thermometers, or any others necessary for the economical and satisfactory operation of the power plant.

Navigating instruments include air-speed meter, altimeter, bank and turn indicators, compass, drift measurer, and the like, with all necessary wiring, piping, mounting, or auxiliary apparatus necessary.

Furnishings cover a multitude of things: Seats, bunks, floors, lavatories, galleys, bins, racks, shelves, etc. Other equipment may be found, such as heating and ventilating systems, wireless, parachutes, soundproof partitions, fire-fighting devices, etc.

The requirements of the military machine are very special and quite diverse. The structural weight is likely to be greater, especially for fighting machines, as these must be put through maneuvers which cause unusually severe loads on the structure. Provision must be made for guns, bombs, torpedoes, their supports, the necessary releasing gear, inter-cockpit phones, wireless, special sighting devices, and the like. Or

cameras and auxiliary equipment may be fitted. Oxygen apparatus for high altitude work, special structure for adapting the plane to the shipboard catapult, special structure to assist in stowing on aircraft carriers are also met with.

A few figures on weight may serve to place these many items in some relation to each other. Unfortunately, we cannot choose a particular basis of comparison for all, as the requirements which are to be met are so varied. The power-plant weight is most important. In freight service we may expect to carry from 3.5 to 5 lb. of pay load per horsepower. The power plant may be as light as half the weight of pay load, or may be 40 per cent. heavier. With relation to the light weight of the plane, it may run from 35 to 55 per cent. The engine weight may run from 2.5 to 1.5 lb. per hp., being greater for smaller and for slower engines, less for the larger and faster. The remainder of the power plant may add 1.5 to 2 lb. per hp. On racing ships or pursuit ships we used to find the engine weight formed two-thirds of the whole power-plant weight. The engine developed roughly 400 hp. and ran at about 2400 revolutions per minute.

With a power plant amounting to 50 per cent. of the light weight (which is high) and a light weight which is 60 per cent. of the total—(also high), the weight of the remainder of the structure, including wings, tail, fuselage and landing gear, becomes about 30 per cent. of the total weight. Considering now the weight of the structure as 100 per cent., we find the parts of the structure have an importance about as follows: The landing gear for a land plane forms 12 to 15 per cent. of the structure; the wings form 40 to 50 per cent.; the tail from 8 to 10 per cent.; the body group from 35 to 40 per cent. Surface controls do not amount to more than 3 per cent. of the weight of the structure.

Of the weight of the fuselage, only a comparatively small portion may be in the actual strength skeleton. For instance, a certain welded steel fuselage, for a pursuit ship weighing 3000 lb. fully loaded, weighed, with engine bearers, less than 150 lb. This amounted to about 15 per cent. of the structural weight. Even in the case of the wings, the structural skeleton may account for only 70 to 75 per cent. of the weight, the rest being cloth covering, dope and paint, and fairings on struts. For a metal-covered wing, the structure may form only 50 per cent. of the whole.

It will be observed that structure is a small portion of the total load, and strength members scarcely make up a majority of the structure. Aerodynamic considerations mean more than weight. It should also be noted that any satisfactory solution of the problem of making the skin on the wings and on the fuselage and nacelles act as a structural member may be expected to contribute a very tidy amount toward reducing weight. One more comment: Paint, varnish, and enamel are a surprisingly large item in the weight of a ship. This is especially true on thin

material. For steel 0.02 in. thick, the weight of finish on both sides required by Navy specifications adds nearly 6 per cent. to the weight. The corresponding increment for aluminum may be as much as 15 per cent. Yet future developments may demand the use of thin material. If we can dispense with a finish, we desire to do so. The Stout airplane, better known by the name of Ford, dispenses with finish entirely on the duralumin sheeting on the wings and fuselage. The insides of tubular members, commonly coated with light varnish by pouring in, shaking, and draining, have been protected by a thin film of oil. The results are said to be satisfactory. To prevent corrosion, mud must be washed off at the ends of trips. No one would consider such treatment advisable in the case of parts made of sheet steel. For many purposes, steel must be available in thin sheets of a stainless alloy equivalent in corrosion resistance, preferably superior, to duralumin.

STRUCTURAL DESIGN

The primary problem involved in the design of a light structure of any sort is that of proportioning the compression members. We must transmit small thrusts long distances. This is especially true in airship design. As this problem demands the use of complicated fabrications of thin material, it rests upon the availability of satisfactory alloys and economical methods of mass production. In large measure the problem is begged at present by the use of simple struts designed according to a modified Euler formula. When Euler's formula is used, soft steel with a modulus of elasticity of 30,000,000 is as light as duralumin with a modulus of about 10,000,000. As alloy steels have a modulus no higher, it is impossible to take advantage of the stronger alloys as long as struts are so proportioned that an Euler-type formula must be used. For long struts the average stress intensity on the cross-section is very low, an undesirable condition.

If higher stresses are used, the component members of a column must be laterally supported at sufficiently frequent intervals so that the stability or resistance to buckling of the whole column or each of its component parts may be great enough to permit using design stresses based on the elastic limit of the material rather than on the modulus of elasticity. This lateral support is normally secured by connecting two rolled structural shapes by diagonal lattice bars. The whole column is permitted an average stress which is a function of the ratio of length to radius of gyration. The distance between lattice points on each component member is made small enough so that the ratio of this length to the least radius of gyration of the component member is less than that for the whole member, the usual specifications requiring it to be not over three-fourths of the ratio for the whole strut. Though this is the practice in building and bridge construction, further refinements in the design are necessary for light construction.

The girder members of airships are at present the best examples of compression members built of several parts latticed together. Yet there is still room for improvement in the design of these members. When lighter gage metal of high strength properties is available, which is adaptable also to fabrication by automatic machinery, possibly by electric welding, and which will retain its high strength properties and corrosion-resisting properties comparatively unimpaired, further important reductions in weight may be secured. In general, it is impossible to give the whole of such a structure a satisfactory heat treatment, so materials that will stand comparatively rough treatment in manufacture without injury are desired. The light column we expect to see may be composed of three or four component members connected together by a primary lattice system, while each component member may be composed of two or more secondary component members latticed together with a secondary system of lattices. If these final components should be of sufficiently thin material, it might even be necessary to resort to corrugations or other equivalent fabrication of the material to give it sufficient stability against buckling.

Columns of which the ratio of length to least radius of gyration exceeds 150 may be designed as Euler struts, subject to all the stress limitations involved, including danger of instability when exposed to vibrations of suitable intensity and frequency. Columns shorter than necessary for a ratio of 40, the amount depending on the stress-strain diagram for the material, may be designed solely with reference to the elastic limit or endurance limit of the material unless intentional or unintentional eccentricities in the material are of considerable amount. Where these are of moderate importance, a diagram of the Tetmajer type has advantages. Professor Junkers found that tests on tubes used as component members were satisfactorily represented by such a formula provided the thickness of the tube was not less than 2 per cent. of the diameter. Where the thickness of the tube was one-third this, numerous small longitudinal corrugations were necessary to make the strength approximate to that given by that formula. With very thin tubes, Professor Junkers found that transverse frames at sufficiently frequent intervals furnished satisfactory lateral support. The primary consideration is that these frames have sufficient rigidity (not strength) to direction-fix (as it is termed) the column at the framing point.

Light Metal Needed

This discussion does not apply to struts only. The design of light metal covering, stiffening bulkheads, compression flanges of beams, all depend on the use of thin material sufficiently dispersed to give a good radius of gyration, yet fastened together often enough to act as a single piece. The complexity of such material would demand rapid

production by automatic machinery for economic reasons alone. Given such material, we may secure weight savings and simplifications in structure which would be of value. Such material would make possible the use of the so-called monocoq type of fuselage construction. This is similar to the so-called Isherwood system of construction used in the construction of ships. The Isherwood system makes the plating of the ship contribute to the effective beam material. The plating is stiffened longitudinally by bulb angles riveted on at frequent intervals. This serves to increase the effective radius of gyration of the plating. The hull is stiffened at frequent intervals along the length by frames, thus reducing the effective column length of the plating to that between the frames. The resulting structure gives the maximum amount of cargo space for given ship volume, and this space is clear of interfering structure from one side to the other. By proper application of these principles, we may build fuselage structures with similar desirable results, and should be able to secure a saving of weight at the same time.

Such material and methods would also offer great possibilities in the design of dirigible balloons. The Zeppelin type of ship depends for its strength on a framed structure. The gas is retained in special fabric balloons. The skin necessary to give a streamline form to the ship contributes nothing to the strength of the ship. On the contrary, a special system of wires is necessary to support the fabric and transmit its loads to the frame. The skin, both exterior and gas retaining, is subject to deterioration at a fairly rapid rate. The gas containers are subject to criticism because of the diffusion losses of gas. This loss is particularly important in military ships using helium. Any system of construction that will permit the use of a metal covering, gastight throughout, capable of sharing the forces in the envelope, would be desirable. In this case weight is an important, but not the only consideration. One other thing might be mentioned. The longitudinal forces in the compression flange of the dirigible envelope, if we may so describe it, are sufficiently small to render advisable the consideration of gas as the prime load-bearing member. This would be accomplished by isolating a portion of gas (or air) in the upper part of the envelope, subjecting it to sufficient excess pressure to resist the forces in that part of the envelope. This is, effectively, what occurs in a dirigible of the non-rigid type. There are certain advantages to be secured, certain disadvantages to be incurred. It is by no means certain that we cannot use such a form of structure to advantage, at least under certain limiting conditions.

There is another contingency to be considered in the case of the dirigible. It may be found advantageous to provide means of heating the gas used for lifting so as to secure additional lifting power. A suggested line of attack would be to provide sufficient lifting force at normal temperatures for the dead load, and aim to run at an elevated tempera-

ture sufficient to balance the added weight of pay load and fuel. There is ample heat available from the engine exhaust of a dirigible as usually powered, supposing we can give the envelope a reasonable resistance to the passage of heat without excessive weight. A double-walled skin, such as might be expected where a metal load-bearing skin occurs, is a suitable place for holding heat-insulation material of proper character. The main difficulty occurs in the heat interchangers, which must be of as light material as possible, yet have sufficient resistance to corrosion from exhaust gases at elevated temperatures. There is no immediate prospect of using such a scheme on any dirigible. The example is given to show possibilities which may be opened up by the provision of material suited to easy and cheap construction, yet possessing qualities suiting it to extraordinarily exacting conditions.

It is obvious that materials meeting the specialized demands of such light and strong structures as aircraft, would, if sufficiently cheap in the fabricated condition, greatly modify methods in many fields. It is not inconceivable that all-metal house construction, for instance, might be rendered economically, esthetically, and comfortably desirable if we could provide a "board" of light metal, insulated and sound-proofed, resistant to corrosion, designed for ease of attachment to a metal frame and for ease of cutting (by special equipment, if necessary), and capable of architectural treatment. It must be remembered that in many respects the aircraft industry is engaged in research work on light construction as far as many other industries are concerned. Methods and materials which at first appear to have but a limited field of use in this special industry sooner or later will be adapted in other places, frequently on a tonnage basis greatly in excess of anything that might be expected of the aircraft industry for many years to come.

Light but Efficient Engines

The aircraft industry has shown how light yet reliable and efficient engines may be constructed for weights as low as 2 lb. per hp. There is now a demand for a light Diesel for aircraft and dirigible work, and this demand will be met in a very few years, not over five at most. The weight of Diesel engines has been lowered sufficiently to permit of their use on trucks even at the present time. Heretofore the lightest Diesels were probably used on submarines. The weight of these engines was not less than 60 lb. per hp., yet published figures on frequency of overhaul would not indicate that this weight is justified on the grounds of increased reliability. Nor is this weight justified on the grounds of cost. It is said that Diesel engines range in cost from \$60 to \$150 per hp. Yet excellent aircraft engines are being sold at \$25 per horsepower.

I quote these particular figures because the contention of the Navy Department has been, during the recent period of criticism, that safety

devices could not be used on submarines owing to weight and space required, which would lead to sacrifice of military features. If the Navy Department would take the time to consult the aircraft industry, it would find that not even the military features of power, speed, and cruising radius are anywhere near what they might be made if the lessons learned in aircraft design and construction were applied to the problem of the power plant alone. It is even possible that these improved military characteristics could be attained without increased cost, judging by the wide discrepancy in engine costs quoted above.

Suitable Materials Should Be Developed

The preceding remarks are intended to encourage the development of materials suited to aircraft purposes. Too frequently we find the point of view that the amount of material that can be absorbed by this industry is too small to warrant special solicitude on the part of the steel manufacturer; yet materials and methods developed by the aircraft industry, or first put to effective use by it, must find wider and wider fields of application, and are finding wider and wider applications. Before the advent of the welded steel fuselage, it was considered quite bad engineering to use a weld where strength in tension is required. Realization is beginning that the monolithic character of a welded frame is a distinct advantage, and that welded joints subject to tension may be made with a high degree of efficiency and reliability, given the necessary control of methods and inspection.

TESTING METHODS

Two points need to be taken up under this heading: (1) methods of determining stress-strain diagrams; (2) determination of the fatigue or endurance limit of materials. If a column formula is to be devised at all scientifically, two considerations must receive adequate attention. First a proper estimate must be made of the probable range in the initial curvature and the probable magnitude of accidental eccentricities. This is largely a question of manufacturing methods, though it is, of course, intimately related to the design. Second the shape of the stress-strain diagram must be considered. It has been noted that the upper limit of strength for a column is a function of the character of the stress-strain diagram for the material. By upper limit is meant the limiting value of the stress at failure for a given fineness ratio (ratio of length to least radius of gyration) as accidental faults become smaller and smaller. The lower limit is also affected but to a smaller extent. A Rankine-type formula fits the points for cast iron very well down to very small values of fineness ratio. A Tetmajer-type formula fits ductile materials much better. The lower limit of stress may be approximated very well by L. B. Johnson's

parabolic formula tangent to the Euler curve, especially for ductile materials. At present it is very difficult to determine the proper method for choosing stresses at failure in the case of certain alloy steels, for the published stress-strain diagrams show an extraordinarily low proportional limit and no real yield point.

Adequate column tests, of course, would be helpful. However, I feel that much could be accomplished by study of the stress-strain diagram. It is usual to report the stress-strain diagram obtained on the first loading of the test piece as the true diagram for the material. I suggest that the information desired is rather the shape of the curve after being loaded and unloaded several times. This would probably require using several test pieces, loading and unloading each several times to a pre-determined extent, and reporting the data so obtained. Except for a column to be tested to destruction on the first loading, the data would better fit the state of affairs in the actual structure and should lead to more reasonable design values for struts.

Fatigue of Materials

The question of endurance limit is closely bound up with the question of shape of the stress-strain diagram. The endurance limit of materials is a question of considerable importance, especially for parts of the structure subject to severe vibration. The determination of this limit requires at present much time and there is available no adequate method for determining the limit by accelerated methods.

There is a method, however, that would bear investigation, and that is one devised by Van Ornum¹ for use on concrete, which gives, on first testing, anything but a straight line even for small stresses. Van Ornum applied axial compressive loads for as many as 60,000 times on a given specimen. Several times during the course of the test he determined the strain diagram from zero load up to the value of the load applied repetitively. He then plotted the curve of modulus of elasticity against the number of times the load had been applied. After an initial period of settling down, the modulus either became and remained a constant, or else slowly decreased after the first period of settling down, the rate of decrease being, for a long time, a very small value approximately constant. When the modulus had fallen to about two-thirds of the value after stability had been reached, the rate of decrease in the modulus began to accelerate at a larger and larger rate until failure occurred. It was found that the greatest applied stress for which the modulus would approach a horizontal line was the endurance limit of the concrete. The value so determined was 50 per cent., very closely, of the crushing strength of the material.

¹ J. L. Van Ornum: The Fatigue of Concrete. *Trans. Amer. Soc. Civil Engrs.* (1907) 58, 294.

Later tests to a much higher number of loadings have only served to confirm this result. It would appear that several runs to 100,000 or less repetitions should furnish some very interesting data on the practicability of using this method for determining the endurance limit on materials of various sorts. Of course, such rapid methods, if valid, would be most valuable in determining endurance limits at elevated temperatures where the natural difficulties are much greater than at room temperature.

PRACTICE IN AIRPLANE CONSTRUCTION

At present it is usual to find wooden beams in the wings. The ribs are a truss construction of wood, although metal ribs aft of the rear wing beam are not uncommon. Streamlined wires are used for the drag trussing, mainly owing to the greater reliability of the end connections and ease of installing. The drag struts are still usually of wood. The leading edge of the wing is frequently, especially on high-speed planes, covered with thin sheet duralumin. The wing fittings are usually of soft sheet steel, cut to shape (and very complicated ones at that) largely at the work-bench, or possibly with the aid of a shaper specially designed for such work. These are bent to shape, reinforcements are welded on, or else spot-welded in place and finished by dip brazing. They may receive a normalizing treatment afterwards. They are then cleaned, galvanized electrolytically, and finished with a baking enamel. At times the desire to lead all loads into the center line of the parts leads to very complicated combinations of bolts and sheet-metal fittings. These fittings require the addition of wooden filler blocks to the wing beams, the fastening bolts passing through the whole.

The tail surfaces are very generally made with a frame of seamless drawn-steel tubing bent to shape and welded together. The ribs may be of thin sheet steel, cut out and bent or flanged to shape. They are usually riveted to the tubes. A recent development has been the arrangement of ribs to form a truss in the plane of the surface, producing a redundant structure materially stiffer than if the ribs were parallel to each other. The tube in the elevator and rudder, which takes both bending moments and torque, may be made of an alloy steel, heat treated, but this precludes the possibility of welding the frame together, so is not usual. Though the customary material is a tubing of S. A. E. 1010 to 1020 steel, there is a tendency to use molybdenum steel tubing at the present time.

The type composition used for tubing is 0.25 to 0.35 per cent. carbon, 0.80 to 1.10 per cent. chromium, 0.40 to 0.60 per cent. manganese, and 0.15 to 0.25 per cent. molybdenum. The tubing is used in the unheat-treated condition. The ultimate strength in tension is about 95,000 lb. per sq. in., while the yield point is 60,000 lb. per sq. in. The material is slightly air hardening, so heated portions of tube near welds tend to regain their original strength on cooling. Butt welds are figured as 84 per cent.

of the strength of the tube. The material is comparatively insensitive to ordinary variations in the heating of the weld. The fatigue resistance and toughness of the steel are particularly high. The material is much more uniform in quality than equivalent alloys of the same strength would be.

The fuselage frame at the present time is made of steel tubing welded together to form Warren trusses. Tubing of the same character mentioned in the preceding paragraph is used. Where the joint distances are not too great, the stronger material may lead to some saving in weight. The main saving in weight has resulted from the substitution of a small amount of weld material for the complicated built-up fittings which were first tried when the tubular frame was being developed. If we represent the weight of tubing required by 100 per cent. (measuring to center lines of all joints), the weight of weld, small stiffening plates, and necessary lugs may represent 5 per cent. after allowing for the weight cut out of the tubes at the joints, while the built-up fittings of type S. A. E. 6100 steel tube to which lugs and plates were welded, together with the necessary belts and rivets, added 15 per cent. after allowing for material removed. The 6100 alloy was dip brazed in some cases, but in all cases was heat treated afterwards. Many fittings cracked before being used.

Interplane struts are made in general of steel or duralumin tubing. The soft steel tubing is preferred, as the plugs with forked ends can be fastened in place by dip brazing. In the case of *N* struts, which are very common, the three tubes used can be easily welded together. Considerable weight is lost on the struts, for the finish and the streamline fairing together weigh about 30 per cent. as much as the strut. As this weight amounts to several pounds, it is probable that a welded steel strut of streamline form would be a satisfactory substitute, especially in the case of quantity production, where it would be practicable to provide dies for giving the strut a taper as well as a streamline form. It is practicable to cut down the air resistance 15 to 20 per cent. by proper tapering, without increasing the weight.

The interplane wires are of streamline form with upset ends, which are threaded. The exact material is not known to me, but the strengths at which the wires are quoted would suggest a S. A. E. 2330 or 3330 steel. The wires have a blue finish produced by the ferro-ferricyanide process, and are then lacquered. They are not made by the individual airplane companies. I believe there is one company only in the United States that makes them.

The forward end of the fuselage in the vicinity of the engine and over the gas-tank compartment is usually covered with aluminum sheets "bumped" to shape. This material is easy to work, is much stiffer than steel for a given weight, and resists corrosion very satisfactorily. Even today the balance of the fuselage cover is cloth, for most planes. Quite

a bit of weight must be added to the structure in formers, usually of wood, but sometimes of sheet metal (duralumin), for the streamline form must be maintained.

It is customary to make the axle tube, which is frequently designed as a cantilever beam subjected to a heavy suddenly applied bending moment, of a high-alloy steel possessing an ultimate tensile strength of 200,000 lb. per sq. in. and an elongation of 5 per cent. in 2 in. in the heat-treated condition. The most commonly used alloys are S. A. E. 2340 and 3140, although alloys of the 3230, *3330, and 6130 varieties have been used with proper heat treatment, and the same classes have been used with not over 0.20 carbon. The addition of molybdenum to any of these steels should be beneficial. An alloy containing 0.34 carbon, 0.67 manganese, 0.77 chromium, 3.07 nickel, and 0.41 molybdenum can be treated to give an ultimate strength of 265,000 lb. per sq. in. with a 240,000 elastic limit and have an elongation of 12.5 per cent., not to mention a very satisfactory value of work to rupture.

The other struts, and parts of the landing gear are of similar materials to such parts for interplane bracing. Wire wheels are of similar character and made by the same companies as those used on automobiles. The design is different, to permit absorbing larger side thrusts without failure. A new type of wheel with brakes is of the disk type, the disks being of duralumin. Until very recently, shock absorbers have been either rubber cords or disks, but special gears of the combined air-cushioning, oil damping recoil type are coming into use. There is no information with regard to materials used, but it is certain that the material must be high-strength alloy steels to keep the weight of such a device within reason. Wheels with built-in shock absorbers have been made, but the weight of the mechanism was considerably in excess of the weight of the same mechanism applied to the axle outside of the wheel. Their primary advantage was on racing ships, where an enclosed shock absorber was an aerodynamic requirement of greater importance than the additional weight.

The surface control parts will usually be designed for manufacture from a carbon steel of the S. A. E. 1020 to 1025 class, the latter being preferred. This material comes in sheets. Horns and brackets can be formed from it on the bench, ready for spot welding with the acetylene torch, and dip brazing. Where higher strength is required, the usual material is an alloy steel with a tensile strength of about 100,000 lb., an elastic limit of 80,000, and an elongation of 17 per cent. in 2 in. The customary material is type 2330, although 3315 and 6130 are satisfactory. This steel may be used as obtained in cold-rolled bars. Similar steels in sheets are usually furnished in 0.15 to 0.20 carbon. Bolts are usually made of the 2330 material.

*S. A. E. system of numbers, but not S. A. E. standards.

MANUFACTURING METHODS AND MATERIALS

Readers must not be unduly alarmed at the extensive use of wood, 1015 sheets, 1025 bars, and 2330 bars or 2320 sheets for airplanes. It has been customary to build planes in small batches. Wood-working machinery, metal-working machines of common standard types, bench tools, and the acetylene torch have been the only devices which the small manufacturer has dared use. If he fails, as many of them have, common machines have a market value second hand. The mechanics he can get are used to the type of sheet-metal jobs available. A single order for 50 machines is a large order, even today. The design of machines is constantly changing, especially when companies are developing experimental machines for the government. Hence the type of structure built and the materials used will be largely of the character described. Steel will not be used in places where complicated forming operations, like corrugating, must be used to develop the strength.

Wherever a metal can be used, where weight is important and stiffness of metal parts is desirable, duralumin will be used if possible. It cannot be welded. A satisfactory method has been devised for making soldered joints, which requires plating of the material with copper at the point where a joint is to be made. One or more plates of other metals must be plated on before the copper can be applied, however, and great care is required not to overheat the material. Where welded joints are desirable, it has been customary to use aluminum sheets. These are primarily used for gas tanks and oil tanks. They are very light. Aluminum sheets are also used where the material is to be hammered, as in making cowlings.

Duralumin is sometimes used in the form of tubes, especially where they may replace comparatively short struts of mild steel tube, provided the additional trouble of providing metal sockets for a riveted connection is justifiable. In general, it is used in angles or channels bent up from sheet metal, riveted at the joints. The heat treatment of duralumin is fairly simple. It is heated in a salt bath for a sufficient length of time, then formed at once. The resulting parts will have acquired full strength and hardness in a few days. By far the greater part is attained in 24 hr. While in the soft state, it is much easier to work than the soft steel.

It must be remembered that the weight of a wooden wing rib 6 ft. long, of truss construction, will be about $1\frac{1}{2}$ lb. Very light weight metal is necessary to compete with wood, for the metal thickness cannot go below a certain amount without danger of buckling. We have not yet reached the time when parts are required in sufficiently large quantities to warrant a large layout for special dies and special machinery to produce a variety of light parts with corrugations, flanges, bulges, and the like; or assemblages of light parts rapidly fastened together effectively.

by gang riveting, automatic riveting, pressure welding, or the like. When mass production is warranted, we may expect an enormous increase in pressed, drop-forged, and die-cast parts. When we can form material cheaply so as to take advantage of its full strength, we may expect a great increase in the demand for suitable high-strength alloy steels in tubes, sheets, bars, forging blanks, etc.

An interesting attempt at cutting certain parts from duralumin sheet has been reported recently from the Naval Aircraft Factory. A suitable die is made of cast iron. The sheet material is placed on a rubber "blanket" and the die is pressed on it. One-half of the die is dispensed with. The results are said to be quite satisfactory.

RELATIVE ADVANTAGES OF WOOD AND METAL

Wood is light, strong, and easily worked with ordinary tools. There is a large amount of experience available and the results of experience have been reduced to standard practice to a very large extent. But wood is variable in strength and quality. It is not homogeneous, nor is its strength in different directions the same. Its weight varies with the temperature and humidity of the air. Used in flying boats, it absorbs sufficient water to seriously modify the taking off and flying ability of the ship. It fails by shattering. Glue joints in plywood and in splices may loosen. A wooden structure requires careful inspection at frequent intervals. Inspections of material during manufacture must be carefully and frequently made. Most important of all from the commercial standpoint is the short life. A plane three years old may be decrepit. Reports on commercial planes that have been coming in recently indicate almost twice as great life for all-metal planes. Development must continue along this line if one of the important items of cost of air transportation is to be brought down.

ALL-METAL CONSTRUCTION

Professor Junkers was probably responsible for the first all-metal plane; in fact, for the first all-iron plane. He was soon obliged, by manufacturing conditions, to modify the design so as to use a combination of iron and duralumin. His iron wing coverings were very difficult to make, and could not utilize more than a small portion of the strength of the material, so he substituted thin duralumin sheets, corrugated to attain sufficient stiffness. Tubes subject to heavy stresses were of iron. (The wings are composed of a multitude of spars just inside the surface of the skin.) Tubes subject to small stresses, which would be too thin if made of steel, were made of duralumin. Lighter struts and lacing members were made of sheet metal deeply corrugated for stiffness. All parts were designed

with the idea of using for a given part the material that would give the most satisfactory combination of strength, weight, and ease of manufacture with the material, shapes, and shop methods available for small-scale production. We must give him a great deal of credit for his extraordinary ability as an engineer. He determined the primary principles upon which a satisfactory metal design must rest; devised novel types of construction embodying those principles in a promising practical form; when necessary, gathered fundamental data on the strength of his structures; evolved a design which was distinctly new, practicable, and effective. In a word, he was a man possessed of a first-rate engineering imagination and the training to make effective use of it. It is a great pity that his suggestions and investigations have scarcely been touched by adequate follow-up work. Certain lines of attack that deserve special attention have been suggested in this paper.

I believe I am correct in stating that there are no other distinctive examples of all-metal planes. Certain companies have produced and are producing all-metal planes, but unfortunately I have no data on their methods of construction or materials. As far as outside appearances go, the skin is of corrugated duralumin, the wings are built of metal on the same general lines as the present wood and fabric wings, using in some cases duralumin throughout, in others sheet-steel wing spars and duralumin ribs, and possibly in rare cases all steel construction. The use of an alloy steel would be rare.

There is an increasing tendency to use sheet duralumin, pressed to shape, for ribs. Extruded duralumin shapes are being developed for wing beams, fittings, etc. There is a tendency to use castings of aluminum alloys instead of built-up fittings of sheet steel for wing fittings and the like. There is a tendency to do away with welding in certain cases and substitute riveted, bolted, or other types of construction. This is probably due to certain difficulties inherent in the construction of tubular steel fuselages and similar structures which have numerous joints in light metal parts. While the various members are being welded into place, there is a decided tendency for the whole structure to weave back and forth. Hence all parts must be held in place in a heavy jig until the welding is finished. Even then it is necessary to keep the material added to the sides in balance, as well as that added to the top and bottom, or the structure will spring excessively on being removed from the jig. There will be some spring in any case, which will require correction if the various parts are to line up properly on the finished ship.

One method of correcting this tendency in large measure would be to make the structure in sections and weld, or otherwise fasten, the sections together. Such attempts as have been made along these lines have shown an advantage, but the added weight of the connections and the added expense have considerably nullified the gain.

There is one other tendency in the use of metal to be noted. Sikorsky has simplified construction methods considerably by making his fuselages and wing beams of duralumin angles and channels, using ordinary lacing for his compound struts, and pairs of angles back to back for his fuselage longerons. There is some increase of the structural weight from this method of construction and choice of material, but this has been offset in considerable measure by the care with which aerodynamic efficiency has been secured, so that the planes as a whole compare very favorably with those of any other manufacturer in general performance characteristics.

PROMISING STEELS

We have not touched on the steels used in airplane motors, as a number of articles on this subject have appeared recently. The Wright Whirlwind engine has been very carefully described, together with the methods of construction and steels used. Though other manufacturers vary from these specifications for specified parts, accounts of the commoner alloys used may be found in books on the airplane engine. Such accounts are much more complete and specific than any this paper could cover in reasonable space. Only one thing need be noted. The tendency is to use as few varieties of steel as possible, using varying heat treatments to secure the range of properties desired. This is primarily a result of the demands of economical manufacture.

Turning now to promising steels, consider first the molybdenum alloys. The claims for this material, or materials, are mainly manufacturing ones: greater ease of machining; much wider temperature tolerances in heat treating; greater uniformity in the resulting product. Excellent strength figures are obtainable with an unusual degree of ductility. Certain of the alloys have shown desirable welding characteristics. We may surely expect to see greater use of these alloys, particularly when mass production develops. The most desirable characteristic of these alloys from the designer's standpoint might well be their high endurance limits under vibratory stresses. These limits are not seriously affected by welding in the class of material so used. In this connection I might suggest that tests on welded tubes subject to alternating axial stresses showed failure through the weld, the endurance limit based on the original tube cross-section being about 16,000 lb. per sq. in. while the original tube had an endurance limit of about 26,000 lb. per sq. in. The material used was the customary seamless steel tube of simple carbon steel. This reduction is serious, so any material that shows less falling off, any welding method that may produce a better weld, merits attention. The gas-welding companies claim that the use of a hydrogen atmosphere about the weld during welding greatly improves the metal in the weld. Tests should be carried out to determine the resistance to vibration of welds so made.

DURALUMIN

The only other outstanding materials of promise are the stainless alloys, both iron and steel. Resistance to corrosion is the great demand of the aircraft industry. Duralumin, in spite of its strength, weight, and stiffness, is not a satisfactory resistor of corrosion. The Navy is particularly emphatic on that point. To be sure, an electrolytic treatment (anodic treatment) has recently come into use, but it must be followed by heavy coats of paint to insure permanency. Films of greases are also suggested to prevent corrosion by keeping the surface free from wetting by water.

Duralumin also suffers from a low endurance limit. Where mild steel has a limit of about 26,000 lb., duralumin has a limit of about 11,000 lb. per sq. in. Furthermore, duralumin does not approach a definite endurance limit even after 100,000,000 cycles of stress. Some tests were run on lugs of sheet metal for receiving streamlined wire terminals, part of duralumin, part of steel. They were of standard form and dimensions in all respects, and the tension in the wire was that to which the wire would be subjected in service. The wire was set into forced vibration by an electromagnet at the midpoint of its length. The duralumin lugs stood the treatment for periods perhaps as great in some cases as 12 hr. The steel lugs did not fail after several days. In searching for the reasons for failure, I determined the inertia forces at the end of the wire perpendicular to the thickness of the plate. (The lugs had small bending strength in this direction.) The stress on the extreme fiber resulting from combining the direct tension with the bending stress was well above 11,000 lb., probably approached 18,000 lb. per sq. in. The duralumin lug should have been slightly thicker than the one of steel for the same endurance. Lack of lateral rigidity in tension members forming part of a structure subject to severe vibrations tends to produce such effects. Minor and major details require investigation for such loads and their effects.

STAINLESS STEELS

The stainless steels require a hard polished surface to develop the stainless property. The degree of stainlessness of the iron when drawn to temper after quenching does not seem to have been determined. This matter demands attention, for the stainless iron has very good strength properties. It is sensitive to heat treatment above 1000° F. However, if drawn to 950° F., we retain practically the full strength, which is 147,000 lb. per sq. in. ultimate in tension; 121,000 lb. per sq. in. for the yield point; yet we secure a 55 per cent. reduction in area, an elongation of 18 per cent. in 2 in., an endurance limit of 40,000 lb. per sq. in. under alternating stresses, and good resistance to shock; yet the temperature

limits need not be close as long as the upper drawing temperature does not exceed 1000° F.

Further information is needed regarding this material when welded without subsequent heat treatment. It has been suggested that the steels have a tendency to corrode in the vicinity of the weld under such conditions.

Where an iron of this type is fabricated with numerous welded joints, especially when the material used is thin sheet metal, it would be desirable to have considerable information on methods of treating the resulting product so as to secure high strength properties without inducing warping. It would appear that heating to 1550° F. for a short time followed by fairly rapid cooling in the air would be equivalent to a quenching operation, which could then be followed by drawing at the proper temperature.

This iron, under suitable conditions, is highly resistant to a 200-hr. salt-spray test, the reported loss being 0.0031 gm. per sq. in., equivalent to less than 0.00003 in. on the thickness at each face. Hence, under conditions to which naval vessels are exposed, this material should be able to compete successfully with all other materials used at the present time, even when unprotected. It would take roughly 3000 hr. to reduce the thickness of 0.01 in. metal by 10 per cent. under severe conditions of exposure to air and salt water.

It would be well to mention, in this connection, that a recent large British dirigible is reported to have had its framework made largely of a stainless alloy of iron or steel. This ship was expected to operate over the ocean on long trips.

COST OF MATERIALS

We have made no mention of cost of materials. Duralumin in small quantities, for one or two machines, fabricated into sheets and tubes, may run as high as 50 c. per pound. Stainless iron has a base price on lots of 2000 lb. (electric furnace) of 20 c., which would mean appreciably higher prices on small lots of fabricated material. It is to be hoped that methods can be developed of producing a satisfactory stainless iron in the open-hearth furnace. Open-hearth alloy steels vary in price with the composition, the range in base price being from 2 c. for structural shapes to 7 c. for some of the alloys such as S. A. E. 3300. Monel metal in cold-rolled sheets has a price of about 50 c. per pound. Nickel sheets run perhaps 10 c. a pound higher. A steel like 5100 modified by adding molybdenum might cost 4½ c. per pound. These figures are only rough guides at best, as it has not been possible to give them all on the same basis. Seamless drawn carbon-steel tubes range in price from 15 to 30 c. per foot depending on the size, the figure corresponding very roughly to 85 c. per pound and 24 c. per pound, respectively. The figures were based on lots of less than 100 ft. So we should not expect a very large percentage

increase in cost of fabricated material even when using a comparatively expensive alloy.

A hasty examination of these cost figures, made in conjunction with a similar review of present practice and manufacturing methods, will only serve to emphasize the fact that small weight savings and consequent gains in pay load have been sacrificed to secure a structure of reasonable cost (considering both material cost and the ease of continuing established and customary modes of manufacture).

In engine building, material cost is not a large item. Even a material cost of \$1 per pound would only account for 8 per cent. of the selling price of a certain engine. Hence a designer of engines is justified in choosing the best material for a particular purpose. The builder of airplane structures must have suitable materials of less cost if he is to secure orders for his planes. A very good three-seater plane can be bought for around \$2500. Compared with three-seater automobiles at less than \$1000, the airplane is relatively very expensive.

Improvement in Materials

The purpose of this paper is to point out to the best of my ability the many problems which have a distinct bearing on the choice of materials. It is useless to hint further at possible materials or methods of construction. You may rest assured that an attempt to follow up any particular suggestion, although it may not lead to the anticipated result, will at least prepare the way for further developments. That is about all that is accomplished with the great majority of work undertaken.

Those who wish to see steel used in increasing quantities in aircraft should note that there is a distinct probability that the metal beryllium may become a raw material of commerce. If the reports of its properties are even partly true, it will be a formidable competitor of steel, and may displace duralumin altogether. It is considerably stronger than mild steel, does not corrode in air, is only about half as heavy as aluminum, and has a modulus of elasticity nearly $\frac{1}{3}$ greater than steel—quite a formidable group of properties.

DISCUSSION

E. A. RICHARDSON.—An article by L. L. Kahn on Stressed Coverings in Naval and Aeronautical Construction, which gives the theory of the strength of such coverings, numerous drawings showing present patented forms of construction that have been developed, together with an analysis of the relative values of various materials now available or which possibly may be made available for aircraft construction, was published by the Association Technique Maritime et Aéronautique.²

²Tech. Mem. 447. Available in translation from the National Advisory Committee for Aeronautics.

J. A. MATHEWS, New York, N. Y.—You referred to molybdenum steel. What specific properties has that been found to show, which make it particularly useful for airplane construction?

E. A. RICHARDSON.—At the present time the primary use is in the form of tubes in the fuselage framework, possibly also in the framework of tail planes. The use of this material has arisen for two reasons. The strength of the material is roughly 90,000 lb. per sq. in. at the elastic limit, which is more than twice that available in ordinary steel tubing, and the material stands welding without much loss of strength. These two reasons have been of primary importance in the use of this material.

Molybdenum was used in the axle tubes of one of the recently designed Bellanca planes. Axle tubes are required to have a tensile strength of about 180,000 lb. per sq. in. Apparently it was used in that case to increase the elongation from the 2 per cent. permitted, to 13 per cent., giving a tougher material for the rather severe service to which axles are subjected.

J. A. MATHEWS.—At one time Mr. Knerr, of the Naval Aircraft Factory, made an elaborate comparison of chrome nickel, chrome vanadium and nickel sheets for use in airplane construction and at that time the chrome vanadium was adopted as the best material available. Has it now been definitely shown by direct comparison that chrome molybdenum is the best?

E. A. RICHARDSON.—I cannot answer that question, but very little chrome vanadium steel is used in aircraft construction at the present time.

The Manufacture of Some Foreign Rails

BY C. W. GENNET, JR., * CHICAGO, ILL.

(New York Meeting, February, 1928)

ANNOUNCEMENT was made in the spring of 1926 that the Boston & Maine R. R. Co. had contracted with the well-known German steelmakers, Messrs. Fried Krupp, for the manufacture of 15,000 tons of basic open-hearth steel rails at the Rheinhausen Works, for delivery to Boston, Mass.

The manufacture of rails in the United States has for many years been almost a national pride, and as this feeling is chiefly the result of a long-time liberal and consistent patronage of American rails by American railroads, it is not strange that this somewhat unusual announcement should arouse more than ordinary interest. Since the end of the World War, the importation of foreign rail has been fairly large, principally because the newly created economic conditions have rendered some American competition more difficult, but the tonnage imported, for the most part, has been made up of small orders for miscellaneous use; and the contract referred to constitutes the largest single importation of foreign rail in over ten years. In 1915, the Algoma Steel Co. of Sault Ste. Marie, Canada, supplied the Illinois Central R. R. with 30,000 tons of rails,¹ and various other American roads with smaller amounts. In 1902, 1903 and 1904, large tonnages of rail from abroad were purchased, the Louisville & Nashville R. R. alone obtaining 30,000 tons from German mills.

It is the object of this paper to present, in what is believed to be a new and concise form, figures showing the production and consumption of rails in the United States, and to record some of the testing and inspection results of the recent Krupp rails; also, to direct attention to two quite unique departures from American practice that were regular features of the Krupp process and which are worthy, it is thought, of careful study.

PRODUCTION AND CONSUMPTION OF RAILS IN THE UNITED STATES

Table 1 shows the tonnage of rail produced in the United States and the amount imported, exported, and consumed by years since 1849. That, evidently, was the first year of record, for the statistics of the American Iron and Steel Institute and its predecessor, the American Iron and

* Manager, Rail Department, Robert W. Hunt Co.

¹ Robert W. Hunt and C. W. Gennet, Jr.: The Nick and Break Test in the Inspection of Steel Rails. *Proc. Amer. Railway Engng. Assn.* (1916).17, 751.

TABLE 1.—*Production and Consumption of Rails in the United States*

Year	Open-hearth	Bessemer	Gross	Tons	Imports	Gross	Tons	Consumption
			Iron	Total		Exports	Total	
1849	-	-	21,712	21,712	61,752	-	-	83,464
1850	-	-	35,360	39,360	142,035	-	-	181,395
1851	-	-	45,181	45,181	202,098	-	-	247,279
1852	-	-	55,784	55,784	263,189	-	-	318,953
1853	-	-	78,450	78,450	320,351	-	-	398,801
1854	-	-	96,443	96,443	303,070	-	-	399,513
1855	-	-	125,816	123,816	136,624	-	-	260,440
1856	-	-	160,730	160,730	166,601	-	-	327,331
1857	-	-	144,570	144,570	192,112	-	-	336,582
1858	-	-	146,171	146,171	81,155	-	-	227,326
1859	-	-	174,513	174,513	74,982	-	-	249,475
1860	-	-	183,070	183,070	130,901	-	-	313,971
1861	-	-	159,480	159,480	79,810	-	-	249,290
1862	-	-	190,993	190,993	9,095	-	-	200,088
1863	-	-	246,221	246,221	18,308	-	-	264,529
1864	-	-	299,436	299,436	127,193	-	-	426,629
1865	-	-	318,118	318,118	56,541	-	-	374,559
1866	-	-	384,623	384,623	105,248	-	-	469,871
1867	-	2,277*	410,319	412,596	145,580	-	-	556,176
1868	-	6,451	445,972	452,423	223,287	-	-	675,710
1869	-	8,616	521,372	529,988	279,609	-	-	809,597
1870	-	30,357	523,214	553,571	356,387	-	-	909,956
1871	-	24,152	568,467	692,619	505,837	297	-	1,197,869
1872	-	83,991	808,866	809,557	473,973	1,062	-	1,365,746
1873	-	115,192	679,520	794,712	231,046	335	-	1,025,423
1874	-	129,414	521,846	651,262	96,706	1,122	-	746,846
1875	-	259,699	447,901	707,600	17,364	1,080	-	723,864
1876	-	358,269	417,114	785,383	256	3,180	-	782,459
1877	-	356,865	296,911	682,776	31	6,547	-	676,160
1878	8,390	491,427	286,295	765,112	9	8,254	-	779,767
1879	8,168	610,682	376,143	993,993	39,417	3,066	-	1,030,544
1880	12,157	552,196	440,859	1,305,212	259,543	958	-	1,563,797
1881	22,515	1,187,770	456,233	1,646,518	344,929	611	-	1,990,836
1882	20,325	1,284,057	203,459	1,507,851	200,113	3,220	-	1,704,744
1883	8,202	1,148,709	57,994	1,214,905	34,801	2,308	-	1,247,398
1884	2,384	996,983	22,631	1,022,188	2,829	6,034	-	1,016,985
1885	4,279	959,471	13,228	976,978	2,169	7,757	-	971,410
1886	4,692	1,574,703	21,142	1,600,537	41,587	2,644	-	1,639,480
1887	17,145	1,101,904	20,591	2,139,640	137,630	549	-	2,276,921
1888	4,698	1,356,277	12,725	1,403,700	63,037	6,908	-	1,459,829
1889	2,988	1,510,057	9,159	1,522,204	6,217	9,325	-	1,519,096
1890	3,588	1,667,837	13,882	1,885,307	204	16,947	-	1,868,564
1891	5,883	1,298,053	8,240	1,307,176	253	11,239	-	1,296,190
1892	5,819	1,537,588	10,437	1,551,844	347	7,982	-	1,544,209
1893	968	1,189,400	6,090	1,136,458	2,888	19,876	-	1,119,470
1894	1,085	1,016,013	4,674	1,021,772	300	13,556	-	1,008,516
1895	697	1,289,628	5,810	1,306,135	1,447	15,599	-	1,291,952
1896	705	1,116,958	4,347	1,122,010	7,795	73,131	-	1,056,675
1897	500	1,644,580	2,872	1,647,892	415	148,221	-	1,500,066
1898	1,220	1,975,702	3,319	1,981,241	200	301,903	-	1,679,538
1899	523	2,270,585	1,592	2,272,700	2,134	277,714	-	1,991,120
1900	1,333	2,383,654	635	2,385,662	1,448	361,619	-	2,025,511
1901	2,093	2,570,816	1,730	2,674,639	1,905	318,956	-	2,557,588
1902	6,029	2,935,392	6,512	2,947,933	63,582	67,666	-	2,943,758
1903	45,054	1,946,756	667	2,992,477	95,555	30,837	-	3,057,195
1904	145,683	2,127,957	871	2,284,711	37,776	416,250	-	1,906,237
1905	183,264	2,192,347	318	3,275,929	17,278	295,023	-	3,098,184
1906	186,413	3,791,459	15	3,977,887	4,943	328,036	-	3,654,794
1907	252,704	3,380,025	925	3,633,654	3,752	338,906	-	3,298,500
1908	871,791	1,349,153	71	1,921,015	1,719	196,510	-	1,726,224
1909	2,256,674	1,767,171	-	3,028,845	1,542	299,540	-	2,725,847
1910	1,751,359	1,884,442	230	3,636,031	7,861	355,180	-	3,290,712
1911	1,676,923	1,C53,420	234	2,822,790	3,414	420,874	-	2,405,330
1912	2,105,144	1,099,926	-	3,227,915	3,780	445,473	-	2,885,222
1913	2,527,710	517,591	-	3,502,780	10,408	460,553	-	3,052,635
1914	1,525,851	323,897	-	1,945,095	22,571	174,680	-	1,792,986
1915	1,775,168	326,322	-	2,204,203	78,525	391,379	-	1,891,349
1916	2,269,600	440,092	-	2,654,518	26,299	540,828	-	2,339,989
1917	2,292,197	533,315	-	2,944,161	9,263	512,669	-	2,440,755
1918	1,945,443	494,193	-	2,540,892	8,705	453,537	-	2,096,060
1919	1,893,250	214,121	-	2,203,843	17,006	652,443	-	1,568,408
1920	2,324,222	142,899	-	2,504,116	45,684	594,628	-	2,055,172
1921	2,027,215	55,559	-	2,178,818	22,048	321,822	-	1,879,044
1922	2,053,000	22,317	-	2,171,778	26,629	277,090	-	1,921,315
1923	2,735,779	25,877	-	2,904,516	29,706	267,409	-	2,666,813
1924	2,307,533	16,069	-	2,453,332	43,358	208,496	-	2,268,194
1925	2,691,823	9,887	-	2,785,257	36,872	151,690	-	2,670,439

*First year of Commercial Production.

NOTE:- The production of rerolled and electric steel rails has been omitted in the above but included in the total produced.

Steel Association (to both of whom I am indebted), fail to disclose earlier figures. The table shows the growth of the iron industry in America; the transition from iron rails to those of Bessemer steel; and clearly marks the beginning and rapid growth of the open-hearth steel process with respect to rails. It should also help to dispel certain fears that may be held regarding the serious effect of the amount of the importations on the industry. In the last 36 years—that is, since 1890—a total of only 637,555 tons of rail has been brought into the United States against 87,710,350 tons actually rolled and 9,767,262 tons exported. Thus, on the average, for every 1000 tons of rail rolled in the United States there have been 7 tons imported and 111 tons exported. The Iron and Steel Division of the United States Department of Commerce has furnished figures showing that from 1890 to 1925 inclusive, the imported rail came from the following countries: 41.7 per cent. from Canada; 24.2 per cent. from Belgium; 24.0 per cent. from Germany; 4.7 per cent. from United Kingdom; 2.6 per cent. from Netherlands; 1.8 per cent. from France.

MANUFACTURE, TESTING AND INSPECTION OF RECENT KRUPP RAILS

The Boston & Maine R. R., largely double tracked, operates a total of 4287 track miles, located principally in the states of Maine, New Hampshire, Vermont and Massachusetts. In those somewhat mountainous New England states, conditions occur which demand a high standard of track maintenance and rail steel. Temperature changes are quite extreme, and the traffic, especially that to which some of the Krupp rail will be subjected, is heavy and dense with slow-speed freight trains alternating with high-speed passenger service. The maximum grade is about 1.45 per cent. and approximately 36 per cent. of the main-line trackage consists of curves. While train movements on main-line curves up to 8.5° are without speed restrictions; on other main-line curves of a maximum of 15° , the speed is limited. The maximum axle loads of the Santa Fé type of freight locomotives used are 62,300 lb. and Pacific type passenger locomotives have axle loads of 54,000 pounds.

The Boston and Maine contract covered 11,000 tons of 100-lb. rail of what is known as the New York, New Haven and Hartford section, and 4000 tons of 85-lb. rail of the A. S. C. E. section. The important features of these sections are shown in Table 2.

The contract provided that the basic open-hearth steel rails were to conform to the specifications of the American Railway Engineering Assn. as adopted on March 12, 1925. These specifications were slightly modified to permit all of the drop tests to be made on pieces resting head up in the drop-testing machine, and as the Krupp drop-testing machine had a tup weighing a metric ton (2204 lb.) the height of the drop test as specified was changed to 17.2 ft. for the 100-lb. rail, and 14.6 ft. for the

TABLE 2.—*Important Features of Two Boston and Maine Sections*

Section.....	WEIGHT PER YARD	
	100-LB.	85-LB.
N. Y., N. H. & H. A. S. C. E.		
Height of rail, inches.....	6	5½
Width of base, inches.....	5½	5½
Width of head, inches.....	2¾	2¾
Thickness of web, inches.....	1 ½	¾
Area head, square inches.....	4.04	3.50
Area web, square inches.....	2.33	1.75
Area base, square inches.....	3.40	3.08
Per cent. metal in head.....	41.4	42.0
Per cent. metal in web.....	23.8	21.0
Per cent. metal in base.....	34.8	37.0
Moment of inertia.....	47.1	30.0
Section modulus (base).....	16.4	12.1

85-lb. rail. In view of the fact that the supports of the Krupp machine were on a solid foundation rather than on springs, as in this country, the testing was probably a little more severe than would otherwise be the case.

The rails were rolled at the Rheinhausen Works from steel made by the straight open-hearth process, in four tilting basic-lined furnaces, each of approximately 120 tons capacity. The charges, mostly all cold, consisted of about 75 per cent. mill scrap and 25 per cent. pig iron made from Swedish and Morocco ore. Furnace operations were stopped when the bath showed the proper carbon content, and as ferromanganese was added to the furnace the only necessary addition to the ladle was ferro-silicon, and no additions were made to the metal in the ingot molds. It required approximately 10 hr. to make a complete melt. Because the teeming ladles were inadequate to hold all of the 120 tons comprising a furnace melt, many of the melts were tapped into two ladles, the metal of each ladle then being considered a heat. The diameter of the nozzle in the ladle was 1.56 inches.

The ingots were bottom cast in groups of four. The molds, slurred with tar, stood on a cast-iron base plate grooved for runner bricks connected to a central riser. The molten steel from the ladle nozzle entered the central riser through a hole 3 in. in diameter and flowed thence through 1½-in. holes in the runner bricks to each of the four molds. The ingots cast were 25 in. square at the bottom and 21 in. square at the top, with 4-in. radii at the corners. The ingots were poured 88 in. high for the 100-lb. rail and 100 in. high for the 85-lb., and weighed respectively about 12,500 lb. and 13,500 lb. It required about 15 min. to bottom pour a group of four ingots, and after approximately 50 min. the molds were taken off and the ingots charged to the pits.

The pits consisted of three groups, each of 20 holes, of the old-style "soaking pits" in which no reheating was possible. For fear, however,

that the steel for these rails would be insufficiently hot for good results in rolling, these rail ingots were charged to other pits consisting of three groups, each of 16 holes, fired with coke-oven gas. Each hole held but one ingot. After about 2 hr. in the pits, the ingots were bloomed and rolled direct into rails.

The blooming was in a two-high 43-in. engine-driven mill, rolling the top end of the ingot first and reducing it in 21 passes, after six turns, to a bloom approximately $8\frac{3}{8}$ by $7\frac{7}{8}$ in. After a top discard of about 12 per cent. and a bottom discard of 5 per cent., the blooms went without reheating into a three-high, $33\frac{1}{2}$ -in. roughing stand and a three-high $33\frac{1}{2}$ -in. finishing stand, both being engine-driven. The blooms received nine passes in the rail mill for the 100-lb. section and eleven for the 85-lb., so that the total number of passes from the ingot to the rail was 30 or 32, depending on the section being rolled. The rails were sawed to length by a single hot saw, cutting each rail slightly long to allow for milling the ends to practically an exact length of 39 ft. It is important to note that there was no hot cambering machine, the rails going on to one of the four hot beds direct from the mill and hot saws, and being neither spaced nor turned while cooling on the hot beds.

Table 3 gives the results of the rolling, inspection and testing of the rails. The inspection was conducted by American inspectors sent abroad for this particular work and it can be assumed, therefore, that the surface inspection of the Krupp rails was in every way comparable with the practice that would be followed at American mills. The testing was in accordance with the requirements of the specification, except as already noted. It is especially significant to observe that no "X-Rayls" were produced. "X-Rayls," it will be recalled, are the result of finding the fracture of at least one of the test pieces from each heat either piped or segregated. This matter is commented upon later at greater length.

Table 4 shows the chemical composition of the Krupp rails. It is mostly in line with American practice, except perhaps that the sulfur content is low. The ability of the mill to keep the carbon content well on the high side of the mean of the specified range is easily recognized.

Table 5 shows the amount of each classification of rail that was shipped. The specification provided for dividing the acceptable rails into six different classes, each identifiable by the color of paint used on the ends. These results on the Krupp rails are at once comparable with results of American practice, and carefully kept figures covering approximately 450,000 tons of rails rolled to this specification at the different mills of the United States² are shown in Table 6 in comparison with those on the Krupp rails.

² C. W. Gennet, Jr.: The New Rail Specifications and Their Results. *Railway Age* (Sept. 4, 1926) 81, 430.

TABLE 3.—*Rolling and Testing Results*

	85-lb.		100-lb.		Total	
	No.	Per Cent. ^a	No.	Per Cent. ^a	No.	Per Cent. ^a
Furnace melts made.....	45		134		149	
Heats cast and rolled.....	88		242		330	
Ingots rolled.....	920		2,807		3,727	
Rails per ingot (nominal)	10		8			
Rails rolled.....	9,119		21,784		30,903	
Rails restraightened (following inspection).....	102	1.1	357	1.6	459	1.5
Cut for flaws.....	4		106		110	
Cut for other reasons..	386		437		823	
Total short rails....	390	4.2	543	2.5	933	3.0
Made No. 2 for flaws....	456		1,421		1,877	
Made No. 2 for other reasons.....	0		31		31	
Total No. 2 rails....	456	5.0	1,452	6.6	1,908	6.2
Rejected account surface defects.....	250		713		963	
Rejected account other reasons.....	10		8		18	
Total rejected (excepting for tests).....	260	2.8	721	3.3	981	3.2
Rejected account failure at drop test:						
"A" rails.....	26		135		161	
"B" rails.....	26		71		97	
"C," etc., rails.....	56		290		346	
Total rejected at drop test.....	108	1.2	496	2.3	604	1.9
Total all rejections.....	368	4.0	1,217	5.6	1,585	5.1
Made "X-Rayls".....	0		0		0	
Heats on which rails failed at drop test:						
"A" rails.....	3		11		14	
"B" rails.....	3		6		9	
"C" rails.....	1		4		5	
Total heats rejected at drop test.....	1		4		5	

^a Percentage of number of rails rolled.

TABLE 4.—*Chemical Composition*

Specified	Obtained				
	85-lb.		100-lb.		Average
	Range	Average	Range	Average	
Carbon.....	Per Cent. 0.62-0.77	Per Cent. 0.63-0.77	Per Cent. 0.69	Per Cent. 0.64-0.77	Per Cent. 0.70
Manganese.....	0.60-0.90	0.66-0.88	0.78	0.61-0.90	0.77
Phosphorus not over		0.04-0.015-0.038	0.029	0.011-0.040	0.025
Sulfur.....		0.020-0.040	0.028	0.017-0.037	0.028
Silicon not less.....	0.15	0.15-0.23	0.18	0.15-0.24	0.19

NUMBER OF HEATS WITH EACH PER CENT. OF CARBON CONTENT

Carbon Content, Per Cent.	Number of Heats Obtained			Remarks
	85-lb.	100-lb.	Total	
0.62	0	0	0	
0.63	3	0	3	
0.64	7	15	22	158 heats = 48 per cent. were below the mean of the carbon range specified.
0.65	6	25	31	
0.66	6	21	27	
0.67	5	13	18	
0.68	8	27	35	
0.69	7	15	22	
0.70	6	4	10	
0.71	12	30	42	
0.72	6	22	28	172 heats = 52 per cent. were above the mean of the carbon range specified.
0.73	7	26	33	
0.74	7	15	22	
0.75	4	24	28	
0.76	3	4	7	
0.77	1	1	2	
Total.....	88	242	330	

TABLE 5.—*Amount of Each Classification of Rail Shipped*
 (As provided for by A. R. E. A. 1925 specification.)

Classification	Ends of Rail Painted	Amount of Rail Shipped					
		85-lb.		100-lb.		Total	
		Pounds	Per Cent.*	Pounds	Per Cent.*	Pounds	Per Cent.*
No. 2 rail....	White	498,812	5.2	1,889,677	7.1	2,388,489	6.6
"X-Rayl"....	Brown	None	0.0	None	0.0	None	0.0
"A" rail....	Yellow	837,373	8.7	2,903,792	10.9	3,741,165	10.4
Less than 39							
ft. long....	Green	636,799	6.6	1,105,562	4.2	1,742,361	4.8
High carbon..	Blue	3,957,539	41.4	10,405,207	39.2	14,362,746	39.8
All other rail.	No paint	3,646,281	38.1	10,242,387	38.6	13,888,668	38.4
Total.....		9,576,804 =		26,546,625 =		36,123,429 =	
		Tons	Lb.	Tons	Lb.	Tons	Lb.
		4,275	804	11.851	385	16,126	1189

* Percentage of total shipped.

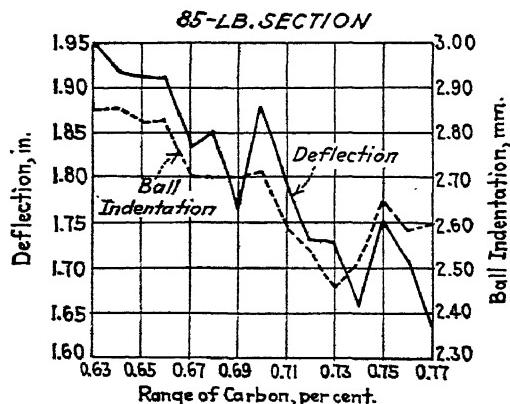
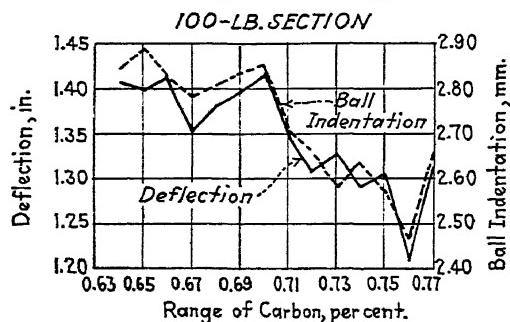


FIG. 1.—GRAPHS OF DEFLECTION AND BALL INDENTATION TESTS.

TABLE 6.—*Comparison of Percentages of Acceptable Rails*

Classification of Rail Shipped	Percentage of Total Shipments	
	Krupp	Average Ameri-can Practice
No. 2 rails.....	6.6	5.8
"X-Rayls".....	None	2.2
"A" rails.....	10.4	12.9
Short length rails.....	4.8	4.1
High carbon rails.....	39.8	30.3
All other rails.....	38.4	44.6

Fig. 1 shows the amount of deflection obtained by the drop tests on the Krupp rails and also the results of the ball indentation tests. Deflection on the Krupp rails are not directly comparable with American practice chiefly because the height of the drop was different and the supports for the test pieces on a solid anvil in one case as against a spring-supported one in the other. The trend of the curves is, however, quite characteristic.

OUTSTANDING FEATURES OF KRUPP PRACTICE

Two notable departures from American practice on rails were outstanding features of the Krupp practice. One was the bottom-casting of the ingots, and the other—perhaps of greater importance—was the fact that all the rails were straightened by passing through a roller straightening machine, the common type of gag press being used only as a last resort for rails that the machine would not make straight.

Notable Results of Bottom-casting

Probably the most important requisite of rails for many years has been their soundness; i. e., the freedom of the metal from pipe and segregation. This matter has been repeatedly discussed, and various devices of ingot practice and of testing have been tried whereby the presence of piping and its accompaniment could be either eliminated or restricted. An extra price is sometimes paid for rails with the understanding that an abnormal top discard, frequently as much as 25 per cent. shall be made for each ingot. Specifications almost invariably have been drawn with some provision whereby the tendency for interior defects in the top rails of ingots could be detected, and the American Railway Engineering Assn. specification, under which these Krupp rails were rolled, requires that a classification known as "X-Rayls" be made of those whose fractured test pieces show interior defects; meaning, chiefly, piping and segregation.

A large tonnage of American rails tested in the past year, previously referred to, showed that on the average 2.2 per cent. of the total shipments were "X-Rayls," but there were none among the Krupp rails. The Krupp ingots were large, in fact heavier, because of being taller, than most American rail ingots; and, according to the inspectors, the steel, for obvious reasons, was poured very hot, yet there was apparently complete freedom from piping. In view of the fact that a great many observations were made of the fractures of "A" rail test pieces, this is indeed a remarkable result, for which bottom-casting must have been largely responsible. In fact, the inspector in charge of the work writes as follows:

Regarding bottom-pouring, after what I have seen here, I am strongly for it. At any rate, there is no other cause to which I can attribute the complete freedom from segregation and piping. Out of over 900 fractured rails which I have examined (to date) at the drop test, we have not found one piped rail; neither have we found any in the yard. . . . Occasionally, in a test piece which broke on the first blow, we would find the appearance of slight segregation, but never sufficient to cause the rails to be classed as "X-Rayls," even if they have not already been rejected. I have made a number of drop tests from pieces cut from the bottom end of the last rail of the ingot but have seen no sign of pipe or segregation. I also found that, as a general rule, these test pieces from the bottom of the ingot stood two more blows before fracture than did the regular test pieces from that heat.

Much has been written on the subject of the bottom-casting of ingots, and opinion of its efficacy apparently varies widely. American steel-makers frequently resort to bottom-casting when making ingots for some special purposes, but as far as known, ingots cast in this manner have not been rolled into rails. With the idea of ascertaining what the possible effect of bottom-casting in this case actually was, small sections were cut from the top end of the top four rails (lettered "A," "B," "C" and "D") and the bottom end of the last two rails (lettered "G" and "H"), all from the same eight-rail ingot, selected at random in the mill at the time of rolling. Sulfur prints were made of these sections and the chemical composition was also obtained on standard drillings (A. R. E. A. practice) from each sample. These results are shown in Fig. 2. While considerable segregation is indicated in the "B," or second, rail, at a location about 22 per cent. from the top of the ingot, the other rails appear almost free from it and also fairly sound physically.

Other of the Krupp rails were analyzed in order to obtain an idea of their chemical condition and the results are given in Table 7. These chemical analyses indicate that segregation is present in these large bottom-cast ingots, possibly to about the same extent as in the shorter and stubbier top-cast American ingots. The number of chemical tests made are also altogether too few, and it is hoped that trials of this method of casting ingots will soon be made with a view to ascertaining much

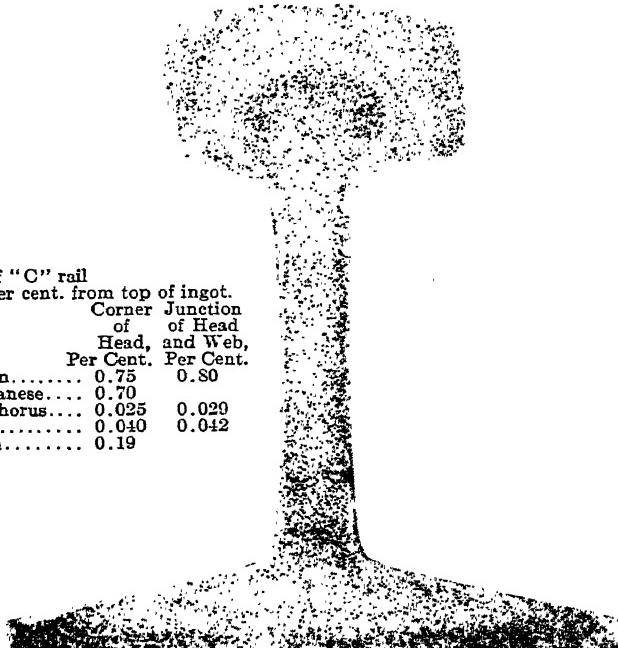
Top of "A" rail
 11.5 per cent. from top of ingot.
 Corner Junction
 of of Head
 Head, and Web,
 Per Cent. Per Cent.
 Carbon..... 0.76 0.77
 Manganese.... 0.74
 Phosphorus.... 0.027 0.029
 Sulfur..... 0.029 0.03S
 Silicon..... 0.21

Top of "B" rail
 21.9 per cent. from top of ingot.
 Corner Junction
 of of Head
 Head, and Web,
 Per Cent. Per Cent.
 Carbon..... 0.71 0.84
 Manganese.... 0.74
 Phosphorus.... 0.027 0.030
 Sulfur..... 0.045 0.04S
 Silicon..... 0.19

FIG. 2.—SULFUR PRINTS OF CROSS-SECTIONS OF KRUPP RAILS.

Top of "C" rail
32.3 per cent. from top of ingot.

	Corner Junction of Head and Web, Per Cent.	Per Cent.
Carbon.....	0.75	0.80
Manganese....	0.70	
Phosphorus....	0.025	0.029
Sulfur.....	0.040	0.042
Silicon.....	0.19	



Top of "D" rail
42.7 per cent. from top of ingot.

	Corner Junction of Head and Web, Per Cent.	Per Cent.
Carbon.....	0.74	0.76
Manganese....	0.68	
Phosphorus....	0.021	0.026
Sulfur.....	0.038	0.036
Silicon.....	0.16	

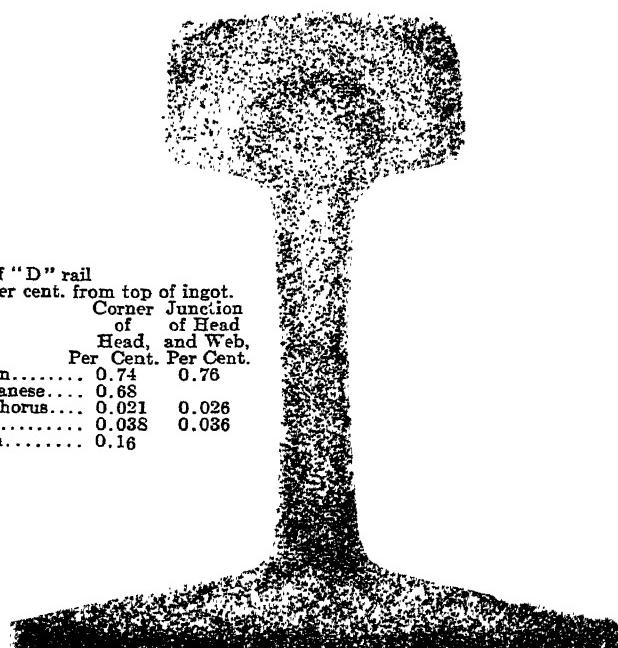


FIG. 2.—SULFUR PRINTS OF CROSS-SECTIONS OF KRUPP RAILS.—(Continued)

Bottom of "G" rail
 84.9 per cent. from top of ingot.
 Corner Junction
 of of Head
 Head, and Web,
 Per Cent. Per Cent.
 Carbon..... 0.74 0.71
 Manganese.... 0.69
 Phosphorus.... 0.024 0.023
 Sulfur..... 0.034 0.034
 Silicon..... 0.17

Bottom of "H" rail
 95.3 per cent. from top of ingot.
 Corner Junction
 of of Head
 Head, and Web,
 Per Cent. Per Cent.
 Carbon..... 0.73 0.72
 Manganese.... 0.71
 Phosphorus.... 0.026 0.025
 Sulfur..... 0.041 0.043
 Silicon..... 0.18

FIG. 2.—SULFUR PRINTS OF CROSS-SECTIONS OF KRUPP RAILS.—(Continued)

more definitely the possible effect on segregation. As far as actual piping is concerned, the practice evidently has much to commend it, and it would not be surprising to find that, with the restricted tendency to pipe, the steel would be freer from segregation.

TABLE 7.—*Chemical Condition of Some Krupp Rails*

Sample from	Drillings from Corner of Head			Drillings from Junction of Head and Web		
	Car- bon, Per Cent.	Phos- phorus, Per Cent.	Sulfur, Per Cent.	Car- bon, Per Cent.	Phos- phorus, Per Cent.	Sulfur, Per Cent.
Top of an "A" rail.....	0.79	0.046	0.045	1.01	0.050	0.029
Bottom of same "A" rail.....	0.72	0.037	0.035	0.86	0.034	0.035
Top of an "E" rail.....	0.75	0.048	0.042	0.69	0.049	0.036
Bottom of same "E" rail.....	0.74	0.050	0.039	0.71	0.050	0.042
Top of an "E" rail.....	0.67	0.050	0.044	0.71	0.055	0.045
Bottom of same "E" rail.....	0.71	0.042	0.050	0.70	0.038	0.042
Near center of a "C" rail.....	0.74	0.033	0.041	0.78	0.038	0.049

Straightening Rails

The standard practice, and the one in use for a great many years, of straightening rails in American mills is to use a gag press having fixed supports about 60 in. apart on which the cold, or hand-warm, rail rests. At the order of the "straightener," sighting the rail from one end, a gag is inserted on the rail between the supports and the moving ram of the press then bends the rail. Thus, by continued effort, the rail being moved lengthwise, and turned, as desired by the "straightener," the proper straightness is obtained quite regardless of the length of the rail. Prior to this straightening process, the rails are passed through a hot cambering machine located between the hot saws and the hot beds. The function of this machine, of course, is to put a curve in the hot rails so that they will be as near straight as practicable when cold, in spite of their unsymmetrical cross-section.

It seems quite unnecessary to comment on the probable abuse, if not actual damage, that a cold rail of high-carbon steel receives when being subjected to the blows of the straightening press, and it is to be remembered that each blow is one well beyond the elastic limit of the metal and that the gag frequently leaves an impression, and perhaps a depression, on the surface of the rail. This cold straightening process is expensive, always requiring a well paid straightener and gagger for each straightening press, the capacity of which may be roughly taken as 100 to 150 tons in eight hours.

The roller straightening machine in use at the Krupp Works consists of three top rolls and two bottom rolls, all power driven, and somewhat

grooved to take a little of the head and base of the rails when head up in the machine. Vertical pinch rolls bearing on both sides of the web of the rails assist to feed the rails through. The general arrangement is as shown on Fig. 3. All of the rolls are moveable and their position is largely dependent on the operator and his idea of the condition of the incoming rail. The whole machine is heavily housed. When rails of a different section are to be straightened, the grooves must be changed in the horizontal rolls, but this is easily accomplished because the grooves are really formed by collars on the main barrel of the roll, which are held on by large lock nuts.

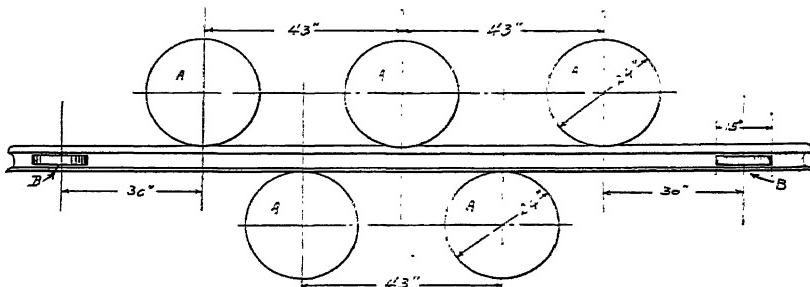


FIG. 3.—ARRANGEMENT OF ROLLS IN ROLLER STRAIGHTENING MACHINE FOR HEAVY STEEL RAILS AT KRUPP WORKS.

A = 24-in. dia. power-driven rolls, slightly grooved for head and base of rails.
B = power-driven pinch rolls.

As previously mentioned, there was no hot cambering machine in the Krupp Works. Consequently, these rails, of which the cross-section was very unbalanced, cooled on the hot beds with a head-low sweep amounting to as much as 12 in. The feed mechanism on the entering side of the roller straightener was nevertheless adequate in every way to meet this condition, with the result that the rails were fed through the machine one after the other fairly fast. It required approximately 15 sec. for a 39-ft. rail to go through the machine, though this time could easily be reduced by running the machine somewhat faster. The temperature of the rails at the time of straightening was apparently of no great importance, and varied about as in this country, from stone cold to slightly warm.

It is obvious, from the arrangement of the rolls, that about 2 ft. of each end of the rail would be largely unaffected. Hence, if a short bend or kink occurred near the end of the rails, it had to be eliminated after roller straightening by going to the customary gag press. Likewise, if there was some condition that the roller straightener did not rectify, the rail was sent to the gag press. From 10 to 20 per cent. of the rails had to be gagged, but if a hot cambering machine had been in use, it is

altogether likely that it would have been necessary to deal with a much smaller proportion.

The rails straightened in this roller machine suffered considerable punishment. Of course, they had been strained well beyond the elastic limit, as was proved by the fact that they were quite free from the usual mill scale on the head and base, excepting at the extreme ends. The author, however, feels that this method of straightening, which could unquestionably be greatly improved by having good hot cambered rails to start with, is likely to be much less detrimental to rails than is the series of from 5 to 15 blows that the average rail receives in a gag press, and also is likely to result in a more accurate line and surface for the finished rail. In short, the very satisfactory results evidently obtained with the roller straightening machine abroad, on these high-carbon and unbalanced-section rails, appears to be a desirable advance in the finishing of rails; and there may be much, from the standpoint of costs as well as improvement of general conditions, to favor the introduction of similar equipment in American mills.

ACKNOWLEDGMENT

The author desires to express his thanks to William Salmon, who was in direct charge of the inspection, and to his assistant, J. C. Kier, for much of the information regarding the manufacture and testing of these Krupp rails for the Boston & Maine R. R. These inspectors were sent abroad for the special purpose of handling this contract in coöperation with others already at the Works, and that they conducted themselves and their work with a fidelity and zeal commensurate with the importance of the commission is a well recognized fact.

DISCUSSION

C. B. BRONSON, New York, N. Y. (written discussion).—The author's paper calls attention in particular to two important and salient features in rail manufacture as applied to foreign rails for use on one American railroad. The first, affecting the physical and structural characteristics of rails, is bottom casting of ingots. The second pertains to roller straightening as a means of reducing the curvature in rails to a true line and surface, which is essential if smooth riding track is to be attained.

While bottom casting of ingots is standard practice at some plants, and used in producing certain articles for railroad service, the writer has no knowledge of this method being used in this country in connection with the production of rails. The principal merit, apparently, as the author indicates, is virtual elimination of pipe. The record of this particular lot of rails is remarkable in this respect. The elimination of segregation is not as thorough, based on the etching data submitted, though these are rather insufficient to draw general conclusions. Yet this point is quite important. A large proportion of head failures, based on many individual investigations, are directly traceable to the chemical and structural unsoundness of the steel influenced by casting conditions. Many "piped" rails are reported as such by nearly every track-

man when he removes a rail but in practically every case the cause of failure is a split head in segregated metal and in no way connected with piping. Elimination of segregation is paramount and if bottom casting of ingots will effect this improvement it will indeed be advantageous. Further experiments would be of material value in settling this point, especially in the casting of ingots for rail steel.

It is well known that the "A," or upper, portion of the small-end-up ingot is more prone to segregation or piping. Some roads specify that the "A" portion of the bloom be discarded and then rolled into tieplates. Others accept the "A" rails as a distinct class and then restrict their service. The percentage of "A" rail-head failures where their installation has been restricted to tangent track is remarkably low, thus showing that, by proper use, rails of this class are not so susceptible to breaking down of the rail head—which is contrary to the rather prevalent belief.

Methods of rail straightening have been widely discussed for the last 40 years or more. The abusive effect of the present practice of gagging has been the cause of comment by many. Others have taken the opposite viewpoint that cold working from overstraining which is essential to reduce the rail curvature has an alleged beneficial effect or at most is not injurious. The impact action or momentary overloading far beyond the elastic limit is of a different magnitude from that ordinarily connected with cold working such as wire drawing, etc.

That gagging may be harmful is realized when consideration is given to the fact that occasionally rails are completely fractured by the application of one blow or impact pressure. Furthermore, specifications recognize the severity of gagging by demanding immediate rejection of any rail which snaps under the applied pressure, readily apparent by sound, which is an indication that the lesser ductile properties within the rail have failed to withstand internal rupture.

Distance between supports has been increased until this is now 60 in., changes have been made in the shape of rams and "gags," and the stroke and speed of application of the bending force have been reduced, but still difficulty from failure of rails in the process continues or recurs.

It is difficult to trace rail failures in service directly back to the effect of gagging. Failure is generally a matter of conjecture and the cause of considerable dispute.

From steelmaking to the final shipment of rails one is impressed with the fact that the plants are marvelously equipped with labor-saving devices, cutting down manual work and fatigue to the minimum except for the tedious and laborious present method of straightening rails. With the rapid increase in percentage of heavier as well as longer rails, the straightener is now placed in a position of even greater disadvantage. Various means are taken to assist him, such as the assignment of a third man at each press to turn the rails or application of mechanical devices. The arduous work continues, however. The straightener has the further disadvantage that it is exceedingly difficult to judge the application of pressure along the rail length and avoid lumping the rail, which is even more injurious from a track standpoint on the sections of great mechanical strength and stiffness.

The principal objections to roller straightening appear to be the following:

1. High initial cost, as the machines must necessarily be massive and rugged.
2. Finishing departments at practically all of the mills would have to be largely revamped or rebuilt, entailing further large expenditures.
3. The curvature of both line and surface of the rails from the hot beds varies and it is questioned as to whether the setting of the rolls in the machine could be made flexible enough for the heavy rail sections.
4. Removal of end kinks or droops could not be accomplished and would thus require a rehandling in a gag press.
5. Perhaps the most serious objection raised is that roller straightening would necessitate the bending and overstraining of every fraction of an inch of the entire

rail length, though it is realized this would be much lower in magnitude than the present method of concentrated heavy impact pressure at several locations in the length of the bar. The practical question is whether a smaller and more uniform pressure throughout the rail length is of lesser or greater severity than concentrated heavy blows.

The question has also been raised as to whether seams or other defects might not be closed up or hidden due to the pressure through the rolls.

These latter questions cannot be fully answered without trial. Some sporadic experiments on a small scale have been made on "T" rail sections but it would seem that more concentrated action is now essential by more elaborate mechanical means and followed by extensive installations in service on a comparable basis of rails straightened through rollers and by use of gagging. The problem is of present importance because of the more extensive use of heavier rails of 39-ft. standard length.

G. F. COMSTOCK, Niagara Falls, N. Y. (written discussion).—Mr. Gennet's paper giving such full details of the method of manufacture of some German steel rails was of great interest to the writer, and the author deserves the thanks of the steel metallurgists in the Institute for presenting to us this information. The writer would question, however, some of Mr. Gennet's implied conclusions and would like to offer the following comments without seeming in any way inappreciative of the value of the paper as a whole.

The suggestion is offered, especially on p. 186, that the absence of what are called "X-Rayls" by the author (although what X-rays have to do with them, I cannot understand) was due to the bottom pouring. This question should be considered in two separate ways, from the standpoint of piping and from that of segregation. In regard to piping the testimony of the inspectors must be considered reliable and conclusive, although it seems most extraordinary that bottom pouring should give less piping than top pouring. When the speed of pouring is noticed, however, another reason for absence of piping at once appears. In several investigations of the problem of piping in titanium-treated rail steel, the writer found that this defect was serious in ingots poured at rates faster than 9600 lb. per min., while with slower pouring the piping was not appreciably greater than in ordinary incompletely killed rail steel. As contrasted with this speed of pouring in American practice, we have in the German practice described by Mr. Gennet a speed of only 3600 lb. per min. distributed among four ingots, from a nozzle of only about $1\frac{1}{2}$ in. dia. Here, then, is undoubtedly the real reason for the lack of deep piping in this steel, and if the speed of pouring were made even nearly as slow as this with top pouring a similar absence of piping would certainly be expected.

In regard to segregation, it would seem from the data offered by Mr. Gennet that the testimony of the inspectors must be questioned. The chemical tests on segregation, which he admits are too few, show in one case 27.8 per cent. segregation at the top of the "A" rail and 19.5 per cent. at the bottom, and in another case 1.3 per cent. segregation at the top of the "A" rail and 18 per cent. at the top of the "B" rail. There is certainly no proof here that segregation was any less in this steel than in ordinary American practice. It seems most likely that the drop-test pieces were so handled at the German mill that the segregation when present was not visible in the fracture and thus was not detected by the inspectors.

It will be very interesting to see how these rails show up in actual service in track, in comparison with American rails, especially in regard to split heads and transverse fissures, and it is to be hoped that this information will be carefully compiled, and published when available.

G. B. WATERHOTSE, Cambridge, Mass.—There is one departure from accepted or usual practice in making rail steel, which was very noticeable in connection with

this order. Mr. Gennet mentioned it, but it may not have been noticed by most of you; it is that very carefully selected, low-phosphorus scrap and low-phosphorus pig iron was in the charge, so that the carbon in the steel was caught coming down, which is different from the general way of making rail steel.

This was a considerable hardship on the people over there. Their supply of low-phosphorus scrap was giving out before they had completed more than half the order. They asked for relief, but it was not granted to them; they were held very strictly to the agreement they had made to use carefully selected scrap and pig iron in each heat. So all the steel was made that way, with very carefully chosen charge, and when carefully melted the phosphorus was low and the carbon was high and the carbon was caught on the way down.

There were some very interesting things connected with the open-hearth practice. The fuel used was a mixture of blast-furnace and coke-oven gas for all this work. The soaking pits, Mr. Gennet mentioned. The ingots were not placed in soaking pits heated with coke-oven gas; as a matter of fact, the pits were heated with blast-furnace gas. I do not know of any other details of practice that may be added except the question of the height mentioned by Mr. Hibbard. I should say the height of the fountain was probably 1 ft. to 18 in. above the molds.

This question of the straightening is very important. The only hot cambering machine in the whole of Europe, so far as I can ascertain, is in a rail mill built in Spain, which was designed by engineers in Philadelphia and built some years ago. The engineers in Europe were not familiar, except such as have been in our country, with the use of hot camber, and, as Mr. Gennet points out, all these rails went through the cold straightening machine without being hot cambered.

I can testify as to the excellent condition of these rails; when they came here they were remarkably straight and certainly as good as any rails we have seen in that respect. Finally, I would like to say that these rails, after approximately 1½ years in the track, are showing excellent results. We cannot say, at this time, that they are showing better results than the good American rails—I do not believe they are—but they are certainly showing very good results.

L. F. REINARTZ, Middletown, Ohio.—I think that the absence of piping undoubtedly has been caused by the fact that the metal had been poured so very slowly. If we had ingots of that size and used a 2-in. nozzle it would take us about 2 min. to prove it. They have taken 15 min. to pour the same mold. You will notice they have an exceptionally small hole in the center runner, 3 in., while in this country it is usually 5 in.; and they also have a 1-in. hole in the runner brick in the bottom, in this country at least 2½ in. is used. So all of those things are going to make it necessary to pour the steel very hot from the ladle but not necessarily hot in the individual mold.

Mr. Comstock brought up a point that you could get the same effect if you top-poured at that rate. That would be practically impossible, because they are pouring with a very small nozzle, 1½ in., and that would cause considerable difficulty in steel practice.

H. D. HIBBARD, Plainfield, N. J.—In this interesting paper piping and segregation are referred to, as they have been by many other writers about steel, as if they were related defects. On the contrary, they are opposites; with one at a maximum, the other is a minimum.

In full piping—that is, perfectly killed steel—segregation is so slight as to be practically negligible in ingots of the size mentioned. The less completely steel is killed, the more it will segregate, as a rule. Partly killed steel segregates more than killed, and rimming steel, which is the antithesis of killed, segregates the most of all.

The method of casting the ingots for these Krupp rails is especially worthy of note, as it seems to be in defiance of usual practice for killed steel such as is mentioned. To avoid piping, killed steel is ordinarily top cast, in molds with wide ends up, and provided with hot tops. But bottom casting gives smoother ingots, freer from laps and splashes; ingots with narrow ends up are easier to strip. the molds last longer, and omitting hot tops saves money.

In the Krupp practice mentioned, all these advantages are secured, without the ingot defects which might be expected, by the use of a small ladle nozzle, so that the rate of filling the molds is exceptionally slow and the time required therefor correspondingly long. During the 15 min. taken to fill a group of molds, solidification goes on, so that, when teeming is finished, metal has solidified around the bottom to a thickness of 3 or 4 in., the frozen shell tapering in thickness toward the top. Thus the still liquid pool of metal has become "larger end up," so that the piping tendency is considerably and effectively checked. The pipe, which must even then be present, may therefore be so short as to be largely or wholly included in the top crop from the rolled bloom. That is an important point.

One point not mentioned in the paper is the height of the central riser, which gives head for forcing the steel into the molds. This becomes an important detail when the group is nearly filled.

Heterogeneity of Iron-manganese Alloys

BY C. R. WOHRMAN, CAMBRIDGE, MASS.

(New York Meeting, February, 1928)

A MELT of pure electrolytic iron with about 0.4 per cent. sulfur and 7 per cent. manganese was prepared in connection with a study of inclusions in iron. The alloy darkened rapidly when etched with a 10 per cent. alcoholic solution of nitric acid, and microscopic examination revealed the presence of a semimartensitic, semi-Widmanstättian structure (Figs. 1 and 2) closely resembling the structures found by Benedicks in his artificially prepared "meteoric iron."¹

The structures found by Benedicks were readily explained by the presence in his alloy of the two well-known iron-nickel solid solutions, taenite and kamacite, and of their eutectoid (?) aggregate, plessite. By analogy, one would infer the existence of similar phases in the iron-manganese alloy just described, such an inference being strengthened by the similarity displayed in many ways by nickel and manganese in their effects on iron.

IRON-MANGANESE ALLOYS ARE REGARDED AS HOMOGENEOUS

Heterogeneity of iron-manganese alloys has not been recognized heretofore, judging from the data of standard metallographic books and those of original papers. In fact, iron and manganese are quite generally regarded as completely miscible in the solid state. Dr. Rosenhain,² for example, writes:

Alloys of group (a), of which those of gold-silver, iron-manganese, and copper-nickel are examples, when allowed to crystallize sufficiently slowly to attain their condition of final equilibrium, present a microstructure exactly similar to that of a pure metal—the homogeneous character of the molten solution is in that case so completely maintained that the microscope cannot detect the presence of any second constituent.

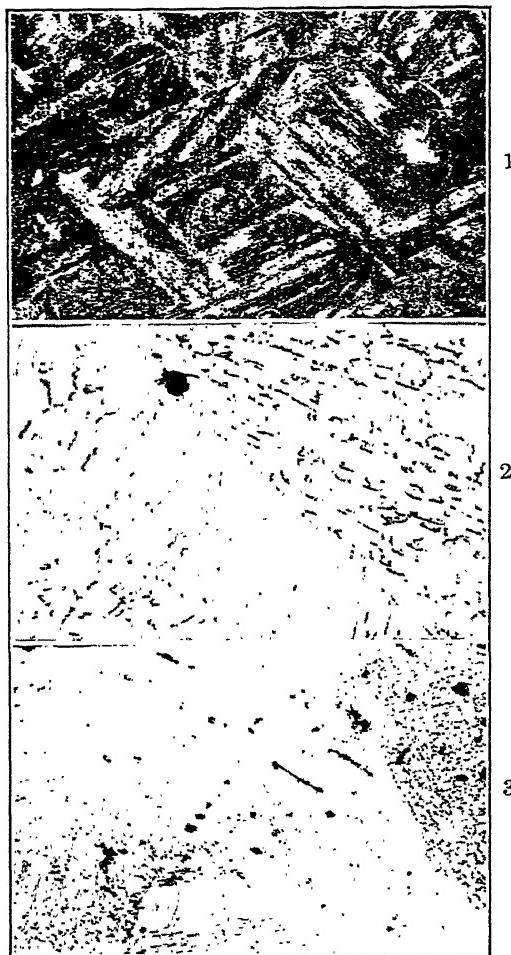
Guillet and Portevin³ refer to the iron-manganese system as an example of the "case of metals completely miscible in the solid state."

¹ C. Benedicks: Metallographic Researches, 110-111. McGraw-Hill Book Co., Inc. 1926.

² W. Rosenhain: Physical Metallurgy, 2d ed., 74. Constable & Co., London. 1915.

³ L. Guillet and A. Portevin: Metallography and Macrometry, 35. Transl. by L. Traverner. McGraw-Hill Book Co., Inc. 1922.

The same is true of Desch and Gulliver.⁴ As early as 1898, Le Chatelier determined "that iron and manganese form a continuous series of solid



1



2

3

FIG. 1.—WIDMANSTÄTTEN STRUCTURES, Fe-Mn-S ALLOY. ETCHANT, $\text{HNO}_3 \times 100$.

FIG. 2.—WIDMANSTÄTTEN STRUCTURE, Fe-Mn-S ALLOY. ETCHANT, 3 PER CENT. $\text{HNO}_3 \times 500$.

FIG. 3.—SPOT WITHIN FIG. 2; CHANGE IN PATTERN AT GRAIN BOUNDARY. $\times 2500$.
(Reduced to $\frac{3}{4}$ original size.)

solutions,"⁵ and the same view has been repeatedly advanced in recent years.

⁴ C. H. Desch: Metallography, 3d ed., 404. Longmans, Green & Co. 1922.

G. H. Gulliver: Metallic Alloys, 4th ed., 332. Charles Griffin & Co., Ltd., London. 1921.

⁵ S. L. Hoyt: Metallography, 1st ed., II, 336. McGraw-Hill Book Co., Inc. 1921.

The testimony in favor of the homogeneity of iron-manganese alloys seems overwhelming, but most of it appears to be based on the evidence presented by Levin and Tammann, who, in 1905, laid down the constitution diagram of the iron-manganese system and stated that "the two metals form a continuous series of solid solutions."⁶ This fact becomes significant when it is remembered that the work of Levin and Tammann was largely of a preliminary character and did not pretend to be complete. In fact, Levin and Tammann merely established the liquidus-solidus curves of the iron-manganese system, employing iron containing 0.07 per cent. C, and examined, rather superficially it appears, a few polished sections of the alloys, noting no evidence of heterogeneity except as a result of dendritic segregation during solidification.

A suggestion that iron-manganese solid solutions may logically be expected to be heterogeneous is found, however, in some of the reports of recent X-ray investigations. E. C. Bain⁷ gives a diagram showing that, in alloys containing 20 to 40 per cent. manganese, both the body-centered and face-centered iron lattices are present, and in alloys containing 60 to 70 per cent. manganese, the lattices of gamma iron and of manganese occur. Westgren and Phragmèn⁸ found that manganese exists in the form of several allotropes, two of which are cubic and relatively stable. This was established also, independently, by A. J. Bradley,⁹ according to whom, "manganese, as ordinarily obtained . . . is likely to contain a mixture of two allotropes in varying proportions." The patterns of the two forms are described by Bradley as "apparently impossible to reconcile with any but the lowest classes of crystal symmetry," which is contrary to the findings of Westgren and Phragmèn.

The mere fact that the iron-manganese alloy described in the first lines of this paper exhibited features similar to those of heterogeneous iron-nickel alloys constitutes, of course, no conclusive proof of the heterogeneity of the former. The presence of two constituents in this alloy is revealed, however, without reasonable doubt, if examination is made at high powers. Fig. 3 shows the two constituents at a magnification of 2500 and also illustrates the discontinuity at the grain boundaries of the patterns in which these constituents appear.

MEANING OF WIDMANSTÄTTIAN AND MARTENSITIC PATTERNS

The Widmanstättian structure of the alloy is itself significant. The term "Widmanstättian" structure (or "Widmanstätten" structure,

⁶ M. Levin and G. Tammann: Über Mangan-Eisenlegierungen. *Ztsch. f. anorg. Chem.* (1905) **47**, 136 *et seq.*

⁷ E. C. Bain: The Nature of Solid Solutions. *Chem. & Met. Eng.* (1923) **28**, 21.

⁸ A. Westgren and G. Phragmèn: Zum Kristallbau des Mangans. *Ztsch. f. Phys.* (1925) **33**, 777.

⁹ A. J. Bradley: Allotropy of Manganese. *Phil. Mag.* (1925) **50**, 1018.

as some prefer to call it) was originally applied to the structures found in meteoric irons. Later, it was extended to similar structures in iron-carbon alloys and has even been used to describe related structures in non-ferrous alloys.

Broadly interpreted, the structure described as Widmanstättian is a "segregate" structure—a structure resulting from the breaking up of a solid phase into two phases, arranged according to more or less regular geometrical patterns, resulting from the mechanism of separation of one of the phases along the crystallographic planes of the mother phase. More specifically, the term applies to the structures resulting from the separation of phases along the octahedral planes of a metal crystallizing in the cubic system.

The significance of the structure known as "martensitic" is essentially the same, the martensitic structure differing from the Widmanstättian merely in being considerably finer, less well defined and less regular (largely on account of the finer grains involved).

In general, then, the presence of a Widmanstättian or martensitic structure in an alloy is *ipso facto* a proof of the heterogeneity of the alloy—the heterogeneity resulting from a separation of phases from a solid mother phase.

In particular, the presence of these structures in the iron-manganese alloy described disregarding the sulfur indicates the presence of several phases formed after the solidification of this alloy.

EXPERIMENTAL MELTS

Of course, the testimony of a single specimen could hardly be taken to establish the heterogeneity of iron-manganese alloys. The remote possibility that the sulfur present in the alloy played some part in the structure developed had to be considered; also the possibility of contamination by carbon. Therefore, three special melts were prepared, of pure electrolytic iron and the purest commercial manganese obtainable. In order to eliminate the corrosive action of manganese, detrimental to both the crucibles and the purity of the melt, it was decided to prepare the alloys in containers of electrolytic iron, placed in turn in alundum crucibles. The manganese, then, would be absorbed by the iron while the latter was still solid or semisolid, and the crucible, upon final melting, exposed to the corrosive effect of the alloyed manganese only, which proved to be negligible.

The electrolytic iron, furnished by the Niagara Electrolytic Iron Co., Inc., was melted in alundum crucibles in an Arsem vacuum furnace and the ingots were allowed to solidify *in vacuo* in the crucibles. Gases dissolved in the iron were thus largely eliminated, and, at the same time, the iron was obtained in a form suitable for the preparation of the con-

tainers desired for alloying. These containers were prepared by simply drilling a suitable hole into the ingots and providing a cover of electrolytic iron.

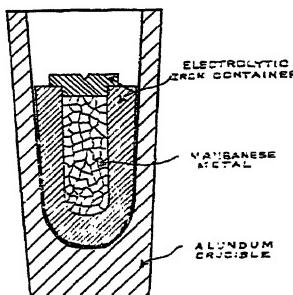


FIG. 4.—CONTAINER USED IN ALLOYING.

After washing the container with xylene and alcohol to remove all traces of oil and other foreign matter, manganese metal was charged into the hole and the iron container was placed in an alundum crucible; the entire assembly (Fig. 4) was then put into the Arsem furnace.

TABLE 1.—*Data Regarding Melts*

Alloy	Charge			Hardness			Remarks
	Material	Grams	Per Cent.	Chemical Analysis*	Rockwell B	Brinell	
Mn-1	Electrolytic Iron	47.1	70.2	Fe 69.54	77.1 (uniform)	155	Non-magnetic
	Manganese	20.0	29.8	Mn 30.34			
Mn-2		67.1		C 0.116			
	Electrolytic Iron	48.7	92.6	Fe 91.85	110.1 (uniform)	390	Magnetic (below 750° C.)
	Manganese	3.9	7.4	Mn 8.05			
Mn-3		52.6		C 0.074			
	Electrolytic Iron	63.1	97.0	Fe 96.65	Top	82.6 S2.6	175
	Manganese	2.0	3.0	Mn 3.32		82.3 62.5	Magnetic
		65.1		C 0.031	Bottom	54.7	105

* The author is indebted for the very accurate analyses to the staff of the Research Department of the American Rolling Mill Co.

† By difference.

Note 1.—The small amounts of carbon found in the melts came, in all probability, from the heating coil of the furnace. The only serious contamination, by 0.116 per cent. C, took place in the case of the high-manganese alloy and becomes, on that account, insignificant. Indeed, the ratio of manganese to carbon, in this alloy, is 261 to 1.

Note 2.—The progressive variation in hardness of the alloy Mn-3 is indicative of a major segregation in this alloy. This, undoubtedly, was caused by the failure to effect homogeneity of the liquid alloy. There is no stirring action in the Arsem furnace; and this particular alloy was kept molten a shorter time than the others, on account of incipient cracking of the crucible.

The melting was done *in vacuo*, the total time required for one melt being about 1 hr. 20 min. Of this, about 40 min. was used to heat the charge to the melting point, and about 30 min. to cool it to about 750° C. The alloys, in two cases, were kept molten for 10 min., during which the temperature was in excess of the melting temperature.¹⁰ In the third case (alloy Mn-3) the incipient cracking of the crucible caused this period to be shortened to 5 min. Upon reaching a temperature of about 750° C. alloys Mn-1 and Mn-3 were removed from the vacuum furnace and placed in an annealing furnace, preheated to 750° C., in which they cooled to room temperature in the course of 14 hr. The alloy Mn-2 was cooled, from about 750° C., in the vacuum furnace in the course of 1.5 hr. Other data of interest are summarized in Table 1.

THE 30-70 MANGANESE-IRON ALLOY (Mn-1)

The alloy Mn-1 (Mn 30.34 per cent.) was found to be non-magnetic and of fairly uniform hardness (Rockwell B 77.1, Brinell 155). Suggestions of a dendritic structure were observed even after coarse polishing with emery paper, the dendrites being clearly revealed after further intermediate polishing. Fig. 5 shows the appearance of the sectioned ingot after this intermediate polish. The dendrites are brought out on account of the greater hardness of the axes, combined with a decided brittleness of the fillings, resulting in easy pitting of the latter.

Fig. 7 shows the grains of the alloy, as brought out by nitric acid etching. The microstructure of the alloy is illustrated by Figs. 9, 10 and 11 and 13, 14, 15 and 16.

At low magnifications ($\times 100$), a structure of the Widmanstättian type is revealed (Fig. 9). The orientation of each of the large grains shown in Fig. 7, governs the depth of the etch which, in turn, influences the clearness with which the structure within the grain is brought out. The orientation of the structure is uniform throughout each grain, and obviously governed by the orientation of the grain. The continuity of the structure within a grain is, however, interrupted locally by ring-shaped areas of a light-colored material, these areas corresponding to the fillings of the dendrites. They are brought out more clearly at a magnification of $\times 500$ (Fig. 10).

Fig. 10, and especially Fig. 11, brings out more clearly the microstructure of the alloy, which is decidedly Widmanstättian in its character. The presence of two phases is conclusively shown, although it is not easy to tell which is which. The heterogeneity is not emphasized by a coloring effect, but is brought out solely because the acid dissolves one of the constituents more readily than the other, namely, the manganese-rich

¹⁰ Facilities for reliable measurements of the temperature in the vacuum furnace were, unfortunately, lacking.

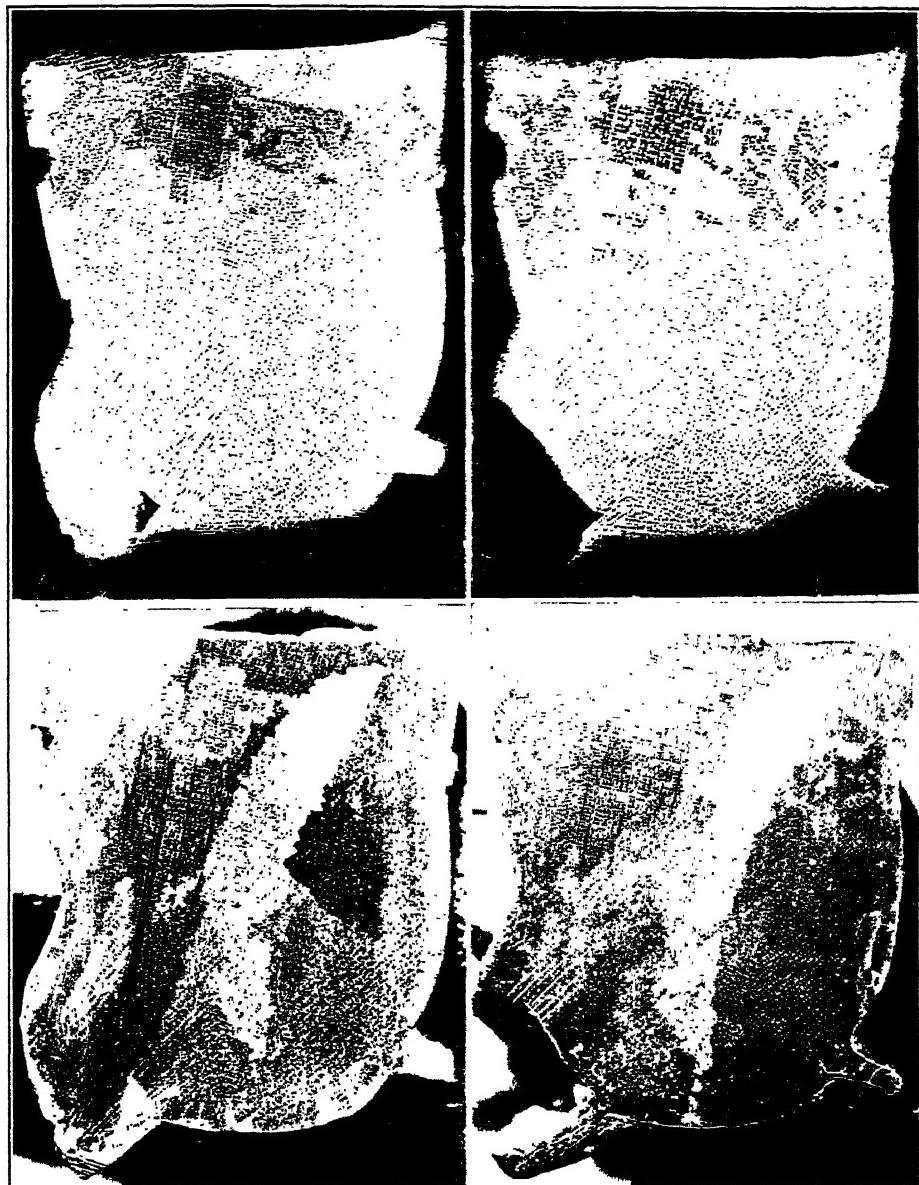
FIG. 5.—DENDRITES IN Mn-1; VERTICAL ILLUMINATION. $\times 3\frac{1}{2}$.FIG. 6.—SAME AS FIG. 5, AFTER ANNEALING. $\times 3\frac{1}{2}$.

FIG. 7.—GRAINS IN Mn-1. OBLIQUE ILLUMINATION. ETCHANT, 3 PER CENT.
 HNO_3 . $\times 3\frac{1}{2}$.

FIG. 8.—SAME AS FIG. 7, AFTER ANNEALING. $\times 3\frac{1}{2}$.

(Reduced to $\frac{3}{4}$ original size.)

constituent, as will be proved later. A relief is thus developed, and the shadows caused by the relief serve to emphasize the heterogeneity. The black lines or areas are shadows, not a separate phase.

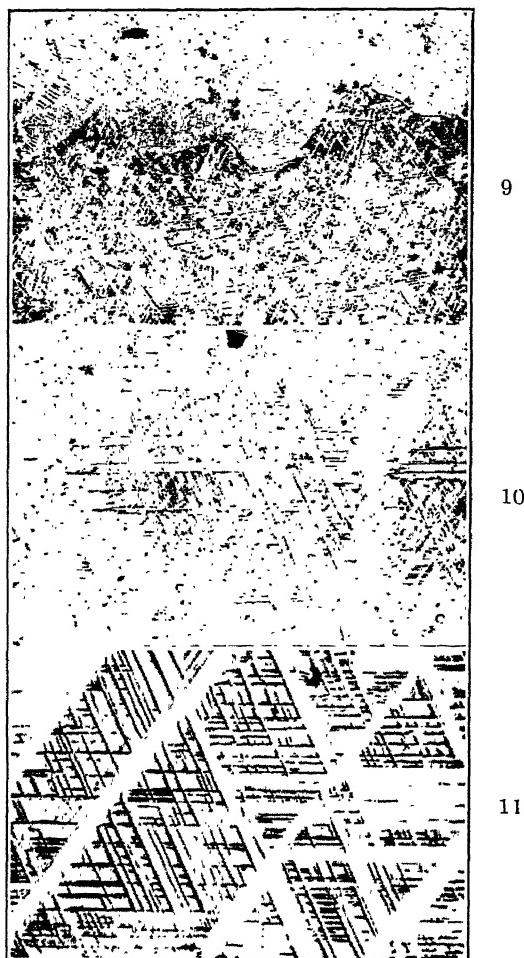


FIG. 9.—ALLOY MN-1; CHANGE IN STRUCTURE AT GRAIN BOUNDARIES. $\times 100$.
 FIG. 10.—ALLOY MN-1. WIDMANSTÄTTIAN STRUCTURE INTERRUPTED BY Mn-RICH DENDRITIC FILLINGS. $\times 500$.
 FIG. 11.—Mn-1. WIDMANSTÄTTIAN STRUCTURE. ETCHANT, 3 PER CENT. HNO_3 . $\times 2500$.
 (Reduced to approximately $\frac{1}{2}$ original size.)

It may, perhaps, not be out of place to illustrate this point by a familiar example which, at the same time, will serve to prove the merits of high magnifications in metallographic work. Pearlite is a constituent of steel familiar to all of us. In etched hypoeutectoid steel, at ordinary

magnifications, it appears as black areas distributed through a light ferritic matrix. At higher magnifications its duplex nature becomes apparent, and at magnifications of $\times 1000$ to $\times 1500$ it is "fully resolved" into what appear to be alternating plates of black and white constituents. Which are ferrite plates, and which the cementite plates? A number of metallo-

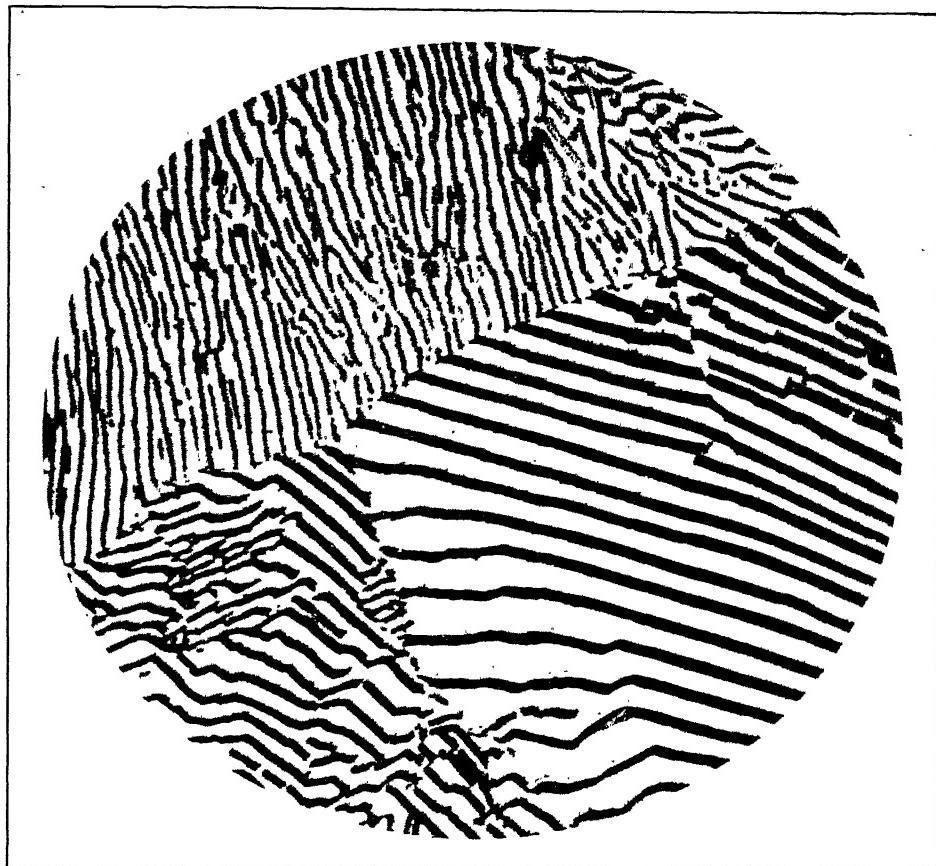


FIG. 12.—PEARLITE. $\times 3000$.
(Reduced to approximately $\frac{3}{4}$ original size.)

graphers seem to be of the opinion¹¹ that the dark plates are ferrite, attacked unduly by the acid on account of their minuteness. We know that the proportion of cementite to ferrite in pearlite is roughly 1 to 7, and Professor Sauveur has repeatedly pointed out that the dark plates fail to agree with this ratio. In fact, the light, supposedly cementite, areas are usually broader than the dark ones, as is well illustrated by

¹¹ A. Sauveur: Metallography and Heat Treatment of Iron and Steel, 3d ed., 50. University Press, Cambridge, Mass. (See Fig. 47.)

Fig. 12, a photomicrograph of pearlite at $\times 3000$. This was taken in the Harvard Laboratory, by F. F. Lucas, who called the writer's attention to the details seen in the light areas and suggested etching features. Are we to assume that cementite will show such etching features on treatment with a weak solution of nitric acid? Certainly not; the light areas showing these features are clearly ferrite and the black areas, of course, are neither ferrite nor cementite, but shadows thrown by the protruding cementite ridges. Note how disturbing influences have broken the cementite ridges in several places while the plastic ferrite exhibits no breaks.

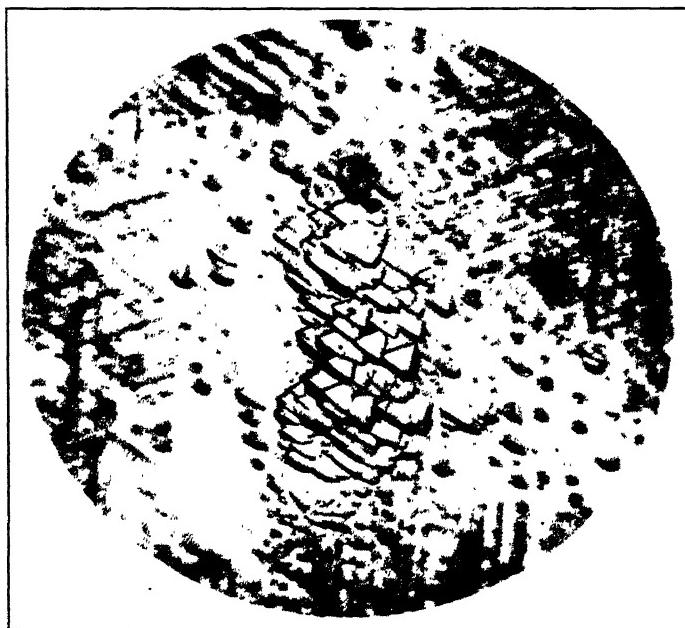


FIG. 13.—ALLOY MN-1, ETCHED 3 MIN. IN 4 PER CENT. IODINE. ETCHING PITS IN MN-RICH PHASE. $\times 500$.

While contrasts due to relief are diminished, true color differences are greatly enhanced by high magnifications and thus, despite the almost identical brilliancy of ferrite and cementite, a distinction between the two becomes possible at high powers. This is apparent on a closer examination of the details in Fig. 12, especially in the upper right side of the photomicrograph. Neither ferrite nor cementite are thus blackened by the acid etch. The ferrite is dissolved by the acid, while cementite is not and the relief developed causes shadows, which are the more marked and the more confusing the finer the structure and the lower the magnification used.

We found in the Mn-1 alloy two phases arranged in a Widmanstättian pattern, one of the constituents being more readily dissolved by dilute nitric acid than the other.

Possibly other etching reagents would serve better to bring out the differences between the two phases. Unfortunately, time did not permit exhaustive experiments in this direction.

However, the effect of a 4 per cent. iodine solution in alcohol was studied to some extent. A two-minute etch with that solution emphasized the dendritic macrostructure, microscopic examination showing that etching pits (see Figs. 13 and 14) had developed in great numbers in the fillings of the dendrites. Etching pits of the same nature, but at



FIG. 14.—SAME AS FIG. 13. $\times 500$.

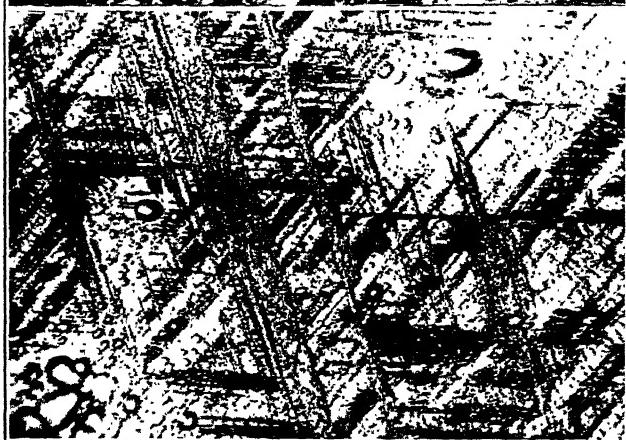
lesser development, were also observed on etching with nitric acid (see Fig. 10). The triangular and hexagonal shapes are typical sections of the cube, therefore cubic symmetry is thus indicated for at least one of the constituents. A further etch of two minutes discolored one of the constituents decidedly, while the other remained bright but exhibited etching pits of the same type as were found in the fillings (Fig. 16). Still deeper etching blackened the dendritic axes, mainly on account of the discoloration to which one of the constituents (largely absent in the fillings) was subject (Fig. 15).

It is *a priori* evident that one of the two phases must be richer in iron than the homogeneous mother phase, and the other richer in manganese; and while one cannot hope to determine, from the evidence on hand, the exact constitution of each of the phases, it ought to be possible to determine which is the one richer in iron, and which the one richer in manganese.

Also, to determine the main characteristics of each. The fact that dendritic segregation took place during solidification proved of great help in answering these questions.



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FIG. 15.—Mn-1. DENDRITIC AXES (DARK) AND FILLINGS (LIGHT WITH PITS). ETCHED 4 MIN. IN 4 PER CENT. IODINE. $\times 100$.

FIG. 16.—Mn-1. IRON-RICH PHASE DISCOLORED. ETCHED 4 MIN. IN 4 PER CENT. IODINE. $\times 500$.

(Reduced to $\frac{3}{4}$ original size.)

Let us visualize the process of solidification of the homogeneous liquid iron-manganese solution. As the alloy begins to solidify, dendritic skeletons are formed of a composition of which the linear crystallization velocity is greatest. The solidification temperature of these skeletons obviously must be higher than that of the mother liquor. (This fact is forcibly emphasized by some of the skeletons actually bridging cavities

near the top of the ingot from which the still liquid metal drained subsequently.) Consequently, the dendritic skeletons, or axes, must be relatively richer in the metal of the higher melting point (iron) and the fillings richer in manganese. Now, Fig. 15 shows the dendritic skeletons to be made up of an aggregate of two phases while the fillings are practically homogeneous. The characteristics of the manganese-rich phase then will be represented more or less accurately by the fillings. From their behavior under polishing, we conclude the manganese-rich phase to be relatively soft and somewhat brittle (pitting). It also is more susceptible to chemical attack, as is shown by the readiness with which characteristic etching pits are developed by dilute nitric acid and especially by iodine. We further note that the iron-rich phase is subject to discoloration by iodine.

Turning again to Fig. 11, we are able to identify the elevated ridges of the aggregate as the iron-rich phase; the depressed areas in between as the manganese-rich phase. In Fig. 16 the former is discolored; the latter abounds in etching pits. We also are able to understand what happens after the solidification of the alloy. The original dendritic grains cease to exist, they "granulate," and the new grains of the still homogeneous solid solution grow rapidly at the high temperatures prevailing. The growth gradually ceases as the temperature falls, the homogeneous solid solution becomes unstable and breaks up into two phases: a solution relatively rich in iron and another relatively rich in manganese. The former separates along the octahedral planes of the mother solid solution in a manner analogous to that of ferrite in slowly cooled hypoeutectoid steel. The two new solutions are both solid solutions of manganese and gamma iron. No further changes on cooling are indicated.

Effects of Annealing

In order to test how readily the heterogeneity due to dendritic segregation may be eliminated by diffusion on annealing, and also to observe what changes, if any, are induced by such annealing, the specimen was heated up to 1025° C. and kept at that temperature for three hours; then it was cooled to room temperature in the course of eight hours.

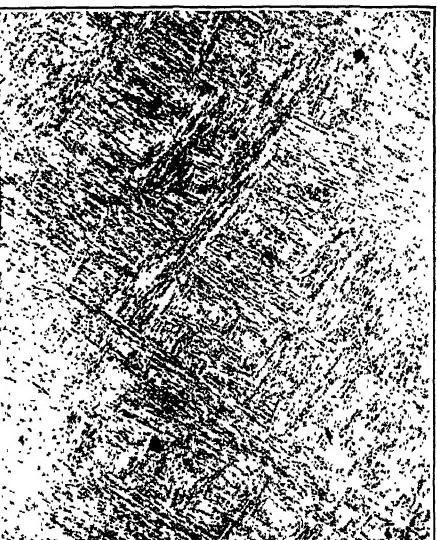
Dendritic segregation persisted in all of its perfection, being revealed, as before, by polishing (Fig. 6). A higher temperature, obviously, is needed to eliminate this segregation. The original grains persisted also (see Fig. 8, and compare with Fig. 7). The temperature region traversed comprised no transformations that would have implied recrystallization, and the temperature of annealing, 1025° C., was apparently too low to permit growth of the grains originally present. The microstructure, too, remained unchanged (Fig. 16).

The stability of this structure can hardly be doubted.

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FIG. 17.—“SQUARES;” WIDMANSTÄTTIAN PATTERNS IN Mn-2. ETCHANT, 3 PER CENT. HNO₃. $\times 100$.

FIG. 18.—“TRIANGLES;” WIDMANSTÄTTIAN PATTERNS IN Mn-2. ETCHANT, 3 PER CENT. HNO₃. $\times 100$.

FIG. 19.—“PARALLEL STRUCTURE;” WIDMANSTÄTTIAN PATTERNS IN Mn-2. ETCHANT, 3 PER CENT. HNO₃. $\times 100$.

FIG. 20.—STRUCTURE CHANGES AT GRAIN BOUNDARIES; WIDMANSTÄTTIAN PATTERNS IN Mn-2. ETCHANT, 3 PER CENT. HNO₃. $\times 100$.

(Reduced to $\frac{3}{4}$ original size.)

THE 8-92 MANGANESE-IRON ALLOY Mn-2.

The alloy Mn-2 was found to be magnetic and to possess the rather startling hardness of 390 Brinell (Rockwell B110.1). These two facts suggested at the outset the presence of constituents different from those found in the previous alloy.

The polished specimen etched with great rapidity in dilute nitric acid, 10 to 15 sec. in a 3 per cent. solution being sufficient to impart a substantial etch (4 to 5 min. were necessary to obtain a satisfactory etch in the previous case). The grain structure revealed [Fig. 21] exhibits numerous

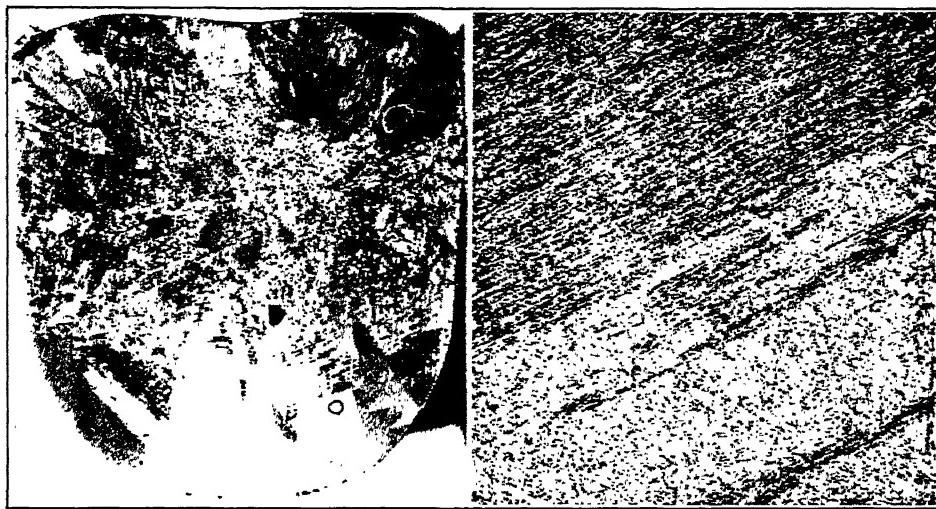


FIG. 21.—GRAIN STRUCTURE IN Mn-2.
NOTE CHANGE IN ORIENTATION WITHIN
INDIVIDUAL GRAINS. $\times 3\frac{1}{2}$.

FIG. 22.—ALLOY Mn-2; SPOT MARKED
IN FIG. 21. $\times 100$.

(Reduced to $\frac{3}{4}$ original size.)

peculiarities. The grains, in general, are quite well defined, but appear to lack homogeneity in crystalline orientation—the very thing that makes a grain a grain. Individual grains are seen to display intercrossing structures exhibiting orientation phenomena, these structures being discontinuous at the grain boundaries, at least in the majority of cases, and thus belonging properly to the grains in which they are found. The conclusion cannot be escaped that the macro-grains seen are the grains of a gamma solid solution no longer existing, the grains proper of the present phases being too minute to be noticeable.

The microstructure at $\times 100$ is illustrated by Figs. 17 to 20 and Fig. 22. The first three photographs were chosen to illustrate the different patterns. Fig. 17 shows a rectangular arrangement; Fig. 18, the more common triangular pattern, and Fig. 19, a parallel structure. The patterns are

very similar to those of the ordinary Widmanstättian patterns; on the whole, however, the structure is more suggestive of martensite. The structures are more or less continuous within one grain and change, ordinarily, quite abruptly at the grain boundaries (Fig. 20). Instances



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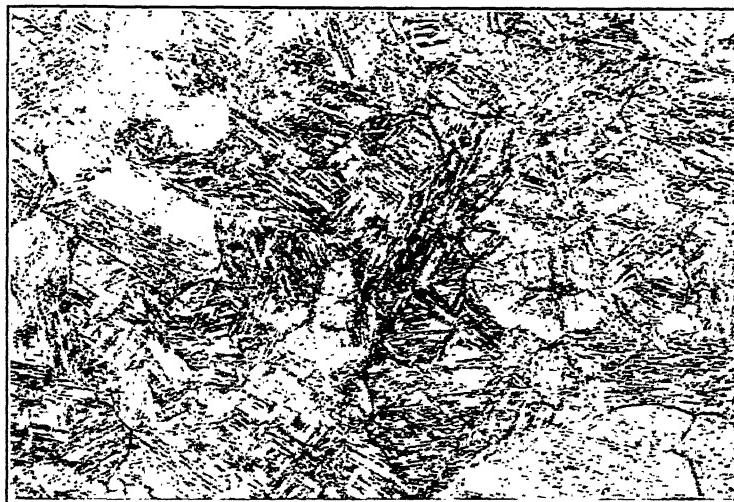
FIG. 23.—DARK AREA OF FIG. 22. $\times 2500$.FIG. 24.—LIGHT AREA OF FIG. 22. $\times 2500$.

where a change in pattern occurs within a "grain" are, however, numerous (Fig. 22).

Higher magnifications (Figs. 23 and 24) fail to supply much additional information but serve to substantiate the heterogeneity of the alloy,

suggesting the presence of at least two different phases. The magnetic qualities of the alloy make it certain that one of the phases is a solution

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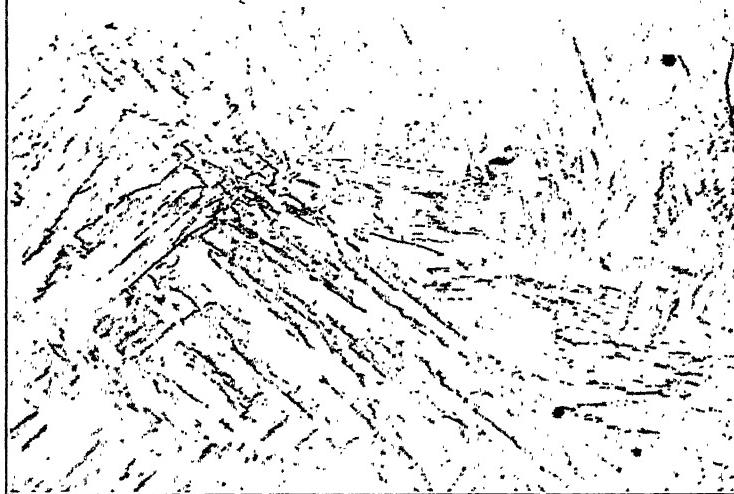


FIG. 25.—ALLOY Mn-2, HEATED AT 950° C. FOR 2 HR. AND QUENCHED. ETCHANT, 3 PER CENT. HNO₃. $\times 100$.

FIG. 26.—SAME AS FIG. 25. $\times 500$.

of manganese in non-gamma iron; an analogue, perhaps, of the troostite of iron-carbon alloys, judging by its hardness and etching characteristics.

Further conclusions about the constituents can hardly be made on the basis of the evidence obtained so far. Two gamma phases may

have been present at first, one or both of which, upon cooling, underwent allotropic changes. It is more likely, perhaps, that there was but one gamma phase—"manganese-austenite," let us say—which, on passing through the critical range, transformed into "manganese-martensite," an aggregate of "manganese-troostite" and "manganese-austenite."

Effects of Heat Treatment

The specimen was heated 2 hr. at 600° C. and quenched in water. No changes were observed in the structure of the specimen but the hardness had decreased slightly (from Rockwell B110.1 to B103.3). The alloy was next heated 2 hr. at 950° C. and quenched in ice-brine. This time the allotropic point clearly had been passed, for the original macro-grains had disappeared and a new set of much finer grains had formed instead.

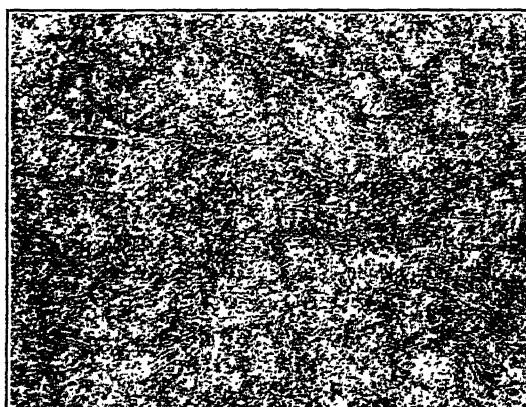


FIG. 27.—NAME AS FIG. 25, ANNEALED 3 HR. AT 950° C. AND SLOWLY COOLED. $\times 100$.

The microstructure remained martensitic (Figs. 25 and 26). The hardness, this time, increased to Rockwell B112.2 (corresponding to 405 Brinell).

An effort was made to locate important thermal points of the alloy, but the somewhat old-fashioned and, perhaps, insensitive apparatus employed for thermal analysis failed to register any such points. Direct testing showed that the alloy lost its magnetism at about 750° C., i. e., at the A₂ point of pure iron.

The specimen, finally, was annealed for 3 hr. at 950° C. and cooled slowly, the interval from 950° to 600° C. being passed in 7 hr. and the remainder in 10 hr. The hardness had decreased somewhat, from 405 Brinell to 360 Brinell, and the microstructure was found to have been refined to a marked degree; remaining, however, martensitic, as before (Fig. 27).

Whatever the nature of the "manganese-martensite," it surely is a far more stable aggregate than martensite itself.¹² The observed changes in hardness suggest, however, quite definitely that "manganese-martensite," on prolonged annealing is softened, "sorbitized" as it were.

THE 3-97 MANGANESE-IRON ALLOY .Mn-3.

The last alloy prepared (Mn-3), containing but 3 per cent. manganese, lacked the uniformity of the two earlier alloys. This was indicated by the hardness test. Indeed, while the hardness near the bottom of the ingot (105 Brinell) scarcely exceeded that of pure iron, it approached the quite substantial hardness of 175 Brinell near the top. The change in hardness was uniform, indicating a similarly uniform change in composition and structure. Etching for 15 sec. with a 3 per cent. alcoholic solution of nitric acid darkened the top two-thirds of the ingot section but left the bottom third relatively bright. The appearance of the ingot (Fig. 42) suggested a pronounced major segregation, the manganese being concentrated in the portions last to solidify. This segregation, in all probability caused by the failure to give sufficient time for the liquid melt to become homogeneous,¹³ was not unwelcome, since it furnished, in a single specimen, the main features of an entire series of alloys, beginning with an alloy of perhaps 0.5 per cent. Mn at the bottom and ending with one of some 5 to 6 per cent. Mn in the region surrounding the pipe.

Fig. 28 illustrates the microstructure in the neighborhood of the pipe. It clearly resembles the martensitic structure of the alloy Mn-2 but shows a greater proportion of light areas. Farther away from the pipe the martensitic structure gets more confused and is broken up by grains of distinctly ferritic appearance, the resulting aggregate being somewhat suggestive of 0.50 to 0.60 carbon steel (Fig. 29). The similarity to pearlitic carbon-steel structures continues to improve, with the increase of the ferritic areas, toward the bottom of the ingot. Fig. 30, for example, could easily be mistaken for a picture of 0.20 per cent. carbon steel. At the very bottom of the ingot a narrow rim of practically homogeneous "ferrite" is observed.

The "manganese-sorbite" of Fig. 30, when viewed at high magnifications (Fig. 32), is seen to consist of an aggregate of two constituents, one of which appears to be identical with the "ferrite" of the ground mass,

¹² I hope I am not offending anyone by referring to martensite as an aggregate. Microscopically, it is evident that martensite is an aggregate, whatever the nature of its constituents may be; for no single phase can exhibit the "segregate" structure peculiar to martensite. Professor Sauveur in his recent contribution to the theory of hardening (*Trans.* (1926) **73**, 859), takes cognizance of this basic fact. Hanemann and Schrader, similarly, make it the very basis of their theory (*Trans. Am. Soc. Steel Treat.* (1926) **9**, 169).

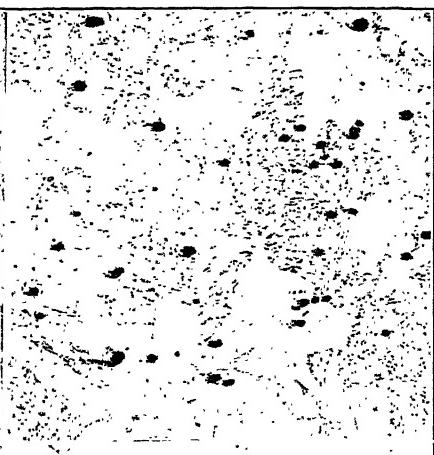
¹³ See Note 2, Table 1.

while the other, appearing, as it does, in the form of protruding ridges and knobs, bears evidence of marked hardness or resistance to acid attack, akin to cementite. This "manganese-cementite" is, undoubtedly, an intermetallic compound of iron and manganese.

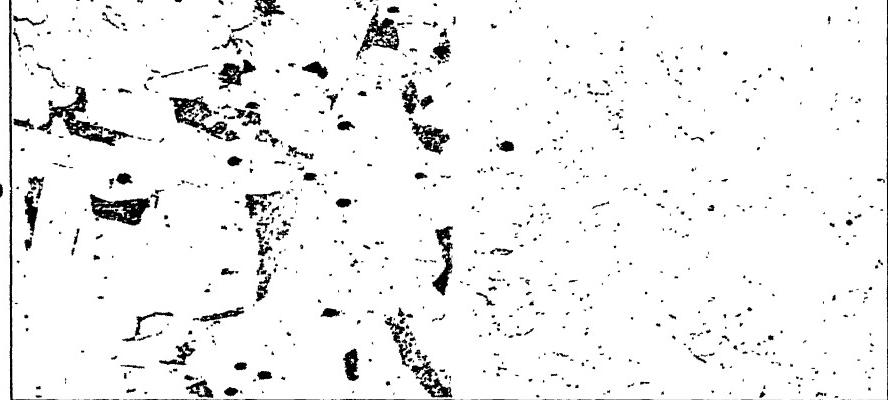
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FIG. 28.—ALLOY Mn-3; STRUCTURE NEAR TOP OF INGOT. ETCHANT, 3 PER CENT. HNO_3 . $\times 100$.

FIG. 29.—ALLOY Mn-3; STRUCTURE TOWARD MIDDLE OF INGOT. ETCHANT, 3 PER CENT. HNO_3 . $\times 100$.

FIG. 30.—ALLOY Mn-3; STRUCTURE TOWARD BOTTOM OF INGOT. ETCHANT, 3 PER CENT. HNO_3 . $\times 100$.

FIG. 31.—ALLOY Mn-3; STRUCTURE AT BOTTOM OF INGOT. ETCHANT, 3 PER CENT. HNO_3 . $\times 100$.

The constituent phases of the martensitic structure near the pipe are revealed at $\times 2500$ in Fig. 33. They are seen to be the same as the ones just described for "manganese-sorbite;" namely, a ferritic ground mass traversed by fences of a resistant constituent, the fences being arranged

in more or less regular geometrical patterns. A breaking down of these patterns, however, can be observed in many places, suggesting that

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FIG. 32.—“Mn-PEARLITE” AREA OF FIG. 30. $\times 2500$.
FIG. 33.—“MARTENSITIC” AREA OF FIG. 28. $\times 2500$.

they are but an inheritance of an earlier system, perhaps the true “manganese-martensite” system, now changed, or partly changed, to a “manganese-pearlite.”

Effects of Heat Treatment

The effects of annealing (3 hr. at 1025° C. followed by slow cooling in the furnace) on the structures just described are of interest. In the

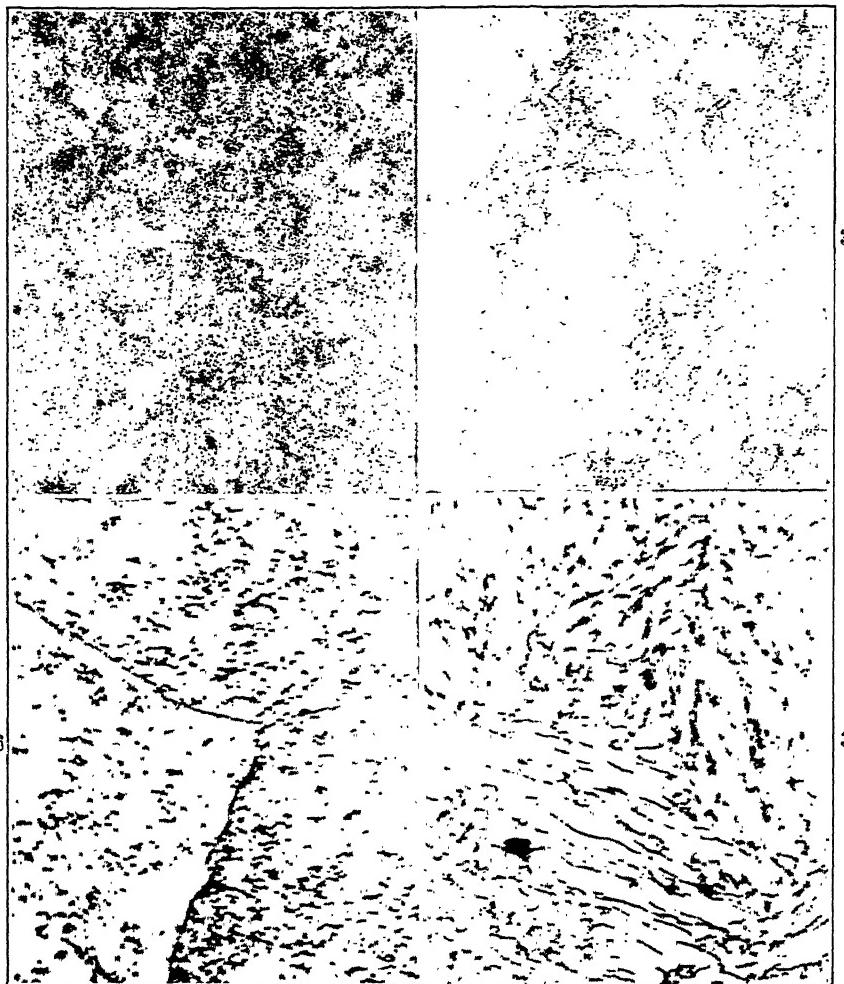


FIG. 34.—SAME AS FIG. 28, AFTER ANNEALING 3 HR. AT 1025° C. ETCHANT, 3 PER CENT. HNO₃. $\times 100$.

FIG. 35.—SAME AS FIG. 30, AFTER ANNEALING 3 HR. AT 1025° C. ETCHANT, 3 PER CENT. HNO₃. $\times 100$.

FIG. 36.—STRUCTURE OF DARK AREAS OF FIG. 35. $\times 2500$.

FIG. 37.—SAME AS FIG. 33 AFTER ANNEALING. ETCHANT, 3 PER CENT. HNO₃. $\times 2500$.

(Reduced to $\frac{4}{5}$ original size.)

first place, the last remnants of dendritic segregation that had originally persisted in the ingot (Figs. 39 and 41) were completely eliminated by

the annealing treatment. (Compare Figs. 39 and 40.) Secondly, the original grain structure was replaced by a new one, the old grains having been completely obliterated in the course of the allotrophic transformations of the alloy.

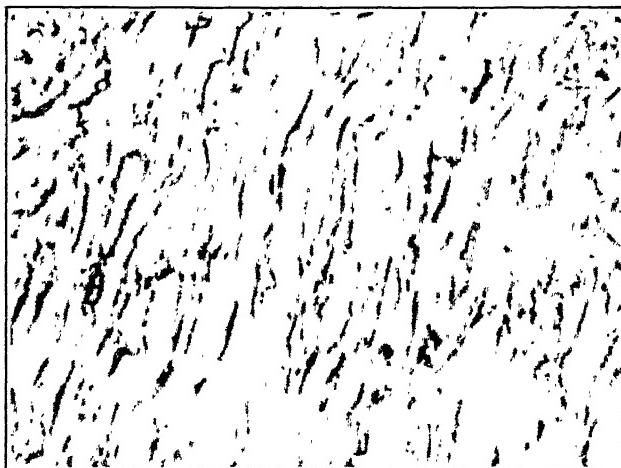


FIG. 38.—“Mn-PEARLITE” RESULTING FROM ANNEALING OF STRUCTURE OF FIG. 28.
ETCHANT, 3 PER CENT. HNO_3 . $\times 2500$.

The major segregation, however, persisted, and the hardness figures still showed a variation from top to bottom. The changes in hardness, effected by the annealing, are best seen in Table 2.

TABLE 2.—*Hardness Numbers of Alloy Mn-3*
Rockwell B Number

	BEFORE ANNEALING	AFTER ANNEALING
Top.....	82.6	88.8
	82.6	88.7
	82.3	80.0
	62.5	59.6
Bottom.....	54.7	44.1

The martensitic structure near the pipe has changed to a sorbitic or pearlitic structure (Fig. 34). Area previously exhibiting islands of a sorbitic constituent in a clean ferritic matrix (Fig. 30) now appear homogenized to a marked extent, the sorbitic constituent having spread into the “ferrite” and become dispersed in it (Fig. 35). Fig. 36, shows these diffused “sorbite” areas at $\times 2500$. They are seen to consist of a ferritic matrix peppered with spheroids of the “manganese-cementite.” The latter is now, clearly, “spheroidized.”

The breaking down of the geometrical patterns, already indicated by the original structure of the “martensitic” area near the pipe, is seen

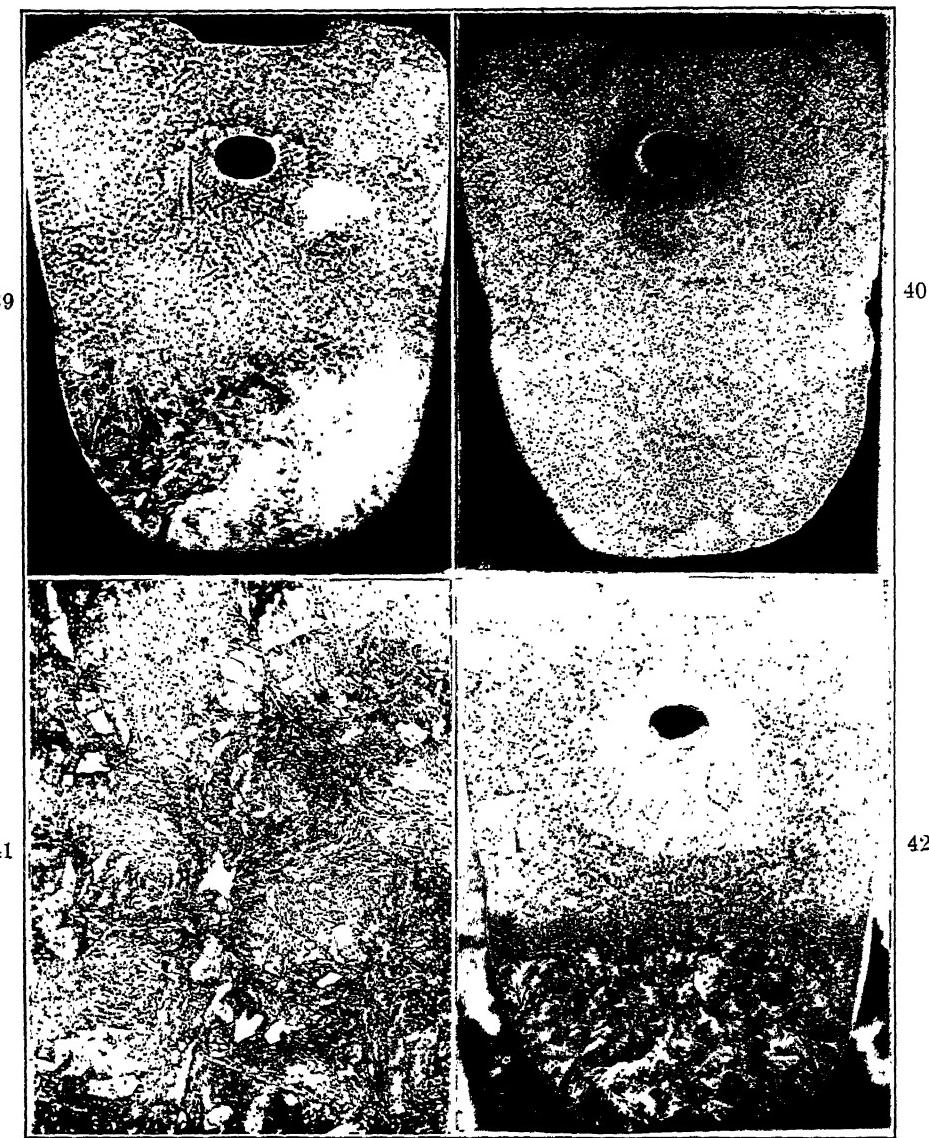


FIG. 39.—DENDRITES IN Mn-3. ETCHED LE CHATELIER; DIRECT ILLUMINATION. $\times 3\frac{1}{2}$.

FIG. 40.—SAME AS FIG. 39, AFTER ANNEALING. $\times 3\frac{1}{2}$.

FIG. 41.—DENDRITIC AXES (OF FIG. 39) RICHER IN IRON (FERRITIC CONSTITUENT). ETCHED LE CHATELIER + HNO₃. $\times 100$.

FIG. 42.—MAJOR SEGREGATION AND GRAIN STRUCTURE IN Mn-3. ETCHANT, 3 PER CENT. HNO₃. $\times 3\frac{1}{2}$.

(Reduced to approximately $\frac{3}{4}$ original size.)

to have considerably progressed during the annealing process. Fig. 37 shows the remnants of a triangular pattern which, before annealing, undoubtedly looked like the one of Fig. 33. Fig. 38 illustrates the final stage approached by these structures—"manganese-pearlite."



FIG. 43.—SAME AS FIG. 30, AFTER QUENCHING. ETCHANT, 3 PER CENT. HNO₃. $\times 100$.

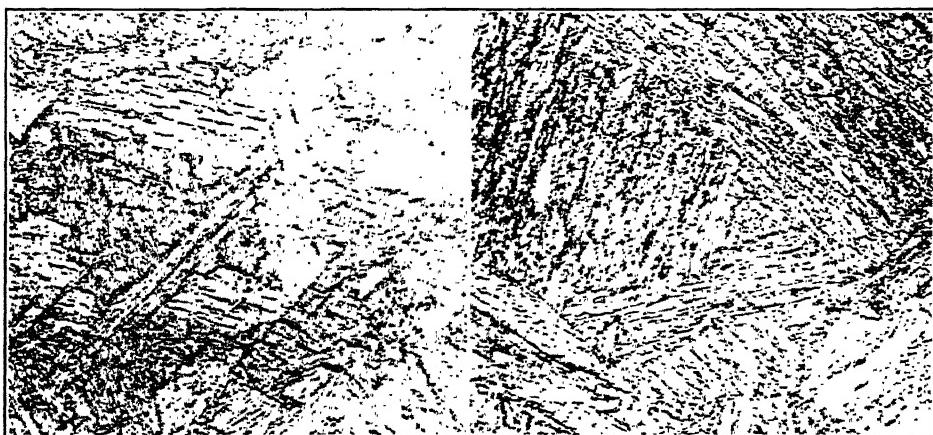


FIG. 44.—"Mn-MARTENSITE" OF FIG. 43. $\times 500$.

FIG. 45.—"Mn-MARTENSITE" CORRESPONDING TO AREA OF FIG. 28, AFTER QUENCHING. $\times 500$.

What is the meaning of all these structures? What is the explanation for them? No definite answer to these questions can be given at the present. The striking resemblance of the iron-manganese structures to iron-carbon structures, however, is suggestive. The heterogeneity of the low-manganese alloy is unquestionable, and it appears that on

thorough annealing an aggregate is formed consisting of a ferritic constituent which probably is a solid solution of a small amount of manganese in alpha iron, and a cementitic constituent which must be a manganese-rich intermetallic compound. It is further suggested that there exists a eutectoid of the two containing about 6 per cent. manganese. The eutectoid appears first in the segregate form of martensite, consisting of phases which break down into "manganese-cementite" and "manganese-ferrite," the aggregate retaining, at first, the martensitic or Widmanst tian pattern, but changing, on continued annealing, to the lamellar form of pearlite. "Manganese-pearlite," however, is less perfect than true pearlite.

This "manganese-pearlite" is capable also of being transformed into "manganese-martensite" by quenching from above the A_3 point. Fig. 43 shows the appearance of the area pictured in Fig. 30 and Fig. 35, after quenching from 950° C. Typical martensite such as is met with in low-carbon steels has developed, as is clearly seen at higher magnifications. (Fig. 44.) Fig. 45 illustrates the appearance of this "manganese-martensite" in the top portion of the ingot that was richer in manganese. Nor has the structure alone changed; the hardness also has changed, in places reaching the figure of 275 Brinell. In particular, the metal of the area pictured in Fig. 43 increased in hardness from 112 Brinell to 265 Brinell (B59.6 Rockwell to B100).

DISCUSSION OF RESULTS

The exact significance of the structures described, the constitution of the phases involved, the mechanism and conditions of formation of the constituents, their regions of stability, and physical properties, the writer was unable to elucidate with any degree of certainty.

An apology is due for the incompleteness of the facts submitted, and the superficial character of the studies presented. The writer, however, had a very limited amount of time at his disposal for these studies, and, knowing that opportunities for further investigations will not present themselves to him in the near future, he presents the evidence obtained in the hope that others may profit from it and develop it.

The one fact of importance that is established without reasonable doubt is the heterogeneity of iron-manganese alloys. Contrary to accepted notions, iron and manganese do not form homogeneous alloys in the solid state, but rather systems of definite constituents, stable within definite temperature and concentration regions.

Another striking characteristic of the iron-manganese alloys is the similarity of their structures to those of the iron-carbon system. The significance of this cannot be overlooked. If we can produce martensitic, troostitic, sorbitic, and related structures by alloying iron with elements

other than carbon, we cannot help concluding that these structures (and their valuable properties), are vested in the iron, or, more strictly, in the solid solutions which iron tends to form, and not in the iron-carbon solutions only, as has been heretofore assumed.

If we stop to consider the matter, it appears, indeed, strange that we should have ascribed to carbon only, the ability to impart to iron the remarkable properties implied by the name "steel." To be sure, we speak of "alloy-steels," and marvel how the properties of such steels are enhanced by the addition of this or the other alloying element but even here, we think of carbon first, for, without carbon, we would have no steel.

The function of the carbon, according to accepted notions, is to create, as it were; that of the alloying elements merely to improve what the carbon has created. The writer knows of no better way to illustrate this point than to refer to the universally accepted views on austenite and austenitic steels. To quote Professor Sauveur,¹⁴

Austenite is universally considered as a solid solution of *carbon*, or of the carbide Fe_3C in gamma iron. All steels above their critical range are made up of this solid solution. While present in all steels above their critical range, much austenite is rarely found in ordinary steels at room temperature even on fast cooling. This is due to the rapidity with which austenite is transformed on cooling . . . The retention of austenite in the cold is greatly *helped* by the presence of some elements, such as manganese and nickel, which lower the position of the transformation range . . . With 10 or more per cent. of manganese and 1 or more per cent. of carbon, or with 25 per cent. nickel, the steel remains austenitic after slow cooling.

Thus we are taught that it is the carbon that *creates* the austenite; the manganese, or nickel, merely *helping* to preserve it at room temperature. It is, naturally, the austenite in austenitic steels that gives them their unusual properties, and austenite, by definition, is "a solid solution of carbon, or of the carbide, Fe_3C , in gamma iron."

Are we justified in ascribing to the 1 per cent. of carbon in Hadfield manganese steel more importance than to the 12 to 13 per cent. manganese present? Are we justified in calling this solid solution "austenite?"

The solid solution, or solutions, that make up Hadfield steel are solid solutions of manganese and carbon in iron, and were we to coin names for them the most important one should be called "hadfieldite" in honor of the inventor of the steel; for the mysterious properties of manganese steel are the properties of "hadfieldite" and some other "-ite" perhaps, not of austenite proper.

Similarly, the properties of high-nickel steels can probably be explained better by the properties of plessite and taenite than by those of austenite. The term "austenitic" as applied to a group of steels containing, in most cases, little, if any, austenite proper, is misleading, unless we re-define

¹⁴ A. Sauveur: Metallography and Heat Treatment of Iron and Steel, 222

austenite as a solid solution of any element or combination of elements in gamma iron.

The two typical facts about austenitic steels are: (1) The iron in them is present in the gamma condition, (2) they exhibit a polyhedral structure. The second feature is not typical of austenitic steels alone, for, as was pointed out by Professor Sauveur, ordinary low-carbon steels (and, of course, pure metals and many alloys other than steel) exhibit this structure also. The term "polyhedral" introduced by Guillet to describe austenitic steels is misleading, therefore.

It would be most logical to refer to austenitic steels as "gamma steels," for the one outstanding fact common to all these steels is the presence of iron in them in the gamma condition. However, a re-definition of the term austenite may prove to be more expedient.

The author's attention was called to the fact that Dr. J. O. Arnold, revolting against austenite,¹⁵ introduced some of the arguments just advanced by the writer. Arnold states:

It is alleged that "austenite" . . . can be retained in the cold by rapid quenching if enough carbon be present. It is also asserted that when so retained it is non-magnetic and identical with iron rich in manganese or nickel, under which latter conditions it is stable at both high and low temperatures . . .

Why iron and manganese, and iron and nickel should be incapable of forming various alloys with special properties depending upon the amount of the alloying element, it is difficult to imagine, except that to admit such a proposition to be possible would seriously damage the dogmatic theories which have now been pushed beyond all reason.

The soundness of Dr. Arnold's criticism is obvious. The severity of this criticism, however, and the fact that it was directed against a perfectly legitimate constituent of steel probably caused it to be dismissed without serious consideration.

In the present paper, it has been shown that manganese, despite its dissimilarity to carbon, is able to *create* structures quite comparable to those usually credited to carbon. It is true, the "manganese-martensite" is not as hard as martensite proper, but it is more stable; the "manganese-pearlite" is not as pretty as true pearlite, but, perhaps, is equally strong and tough.

Perhaps some will suggest that the traces of carbon revealed by chemical analysis of the alloys are responsible for the observed structures, rather than the manganese. To them the writer can only suggest that they prepare corresponding alloys without manganese and observe the resulting structures. It takes a certain number of bricks to build a given structure; there are plenty of manganese bricks in the alloys to do

¹⁵J. O. Arnold: Uniform Nomenclature of Iron and Steel. *Jnl. Iron Steel Inst.* (1910) 81, No. 1, 185 *et seq.*

it with, and far too few carbon bricks. The presence of the structure is a proof that it was built essentially of manganese bricks.

Manganese, without doubt, is not the only element besides carbon capable of creating solid solutions of desirable properties with iron. The author ventures to suggest that all elements that have been found to improve steel form such solid solutions. The valuable properties of some of these solutions are enhanced, unquestionably, by the presence of carbon. Can we be sure that some of them might not, on the contrary, be harmed by carbon?

Steel, in the last analysis, is made possible by the fact that iron exists in at least two well defined allotropic forms possessing a definite and accessible transformation range, and the fact that the physical properties of these two allotropic varieties, especially as regards their capacity for dissolving carbon, are widely divergent. This is a true statement, but a limited one. A more general statement, perhaps equally true, would read:

Iron alloys of remarkable properties are made possible by the fact that iron exists in two well defined allotropic forms possessing a definite transformation range, and the fact that these two allotropic varieties have widely divergent physical properties, especially as regards the solubility in them of alloyed elements.

It is, perhaps, true that the hardness of any "special-martensite" is directly related to the differences in solubility of the special element in gamma and in alpha iron: i. e., the smaller the solubility in alpha iron in proportion to the solubility in gamma iron, the harder the martensite, etc. This, of course, is merely a speculation, but, nevertheless, indicative of the generalizations which a thorough study of the binary alloys of iron may well reveal.

The necessity for a detailed study of the great number of possible binary alloys with iron is indicated. In fact, without such a study we cannot hope ever to understand the mysteries still surrounding some of the important tertiary and quaternary alloy steels which have become an integral part of the civilization of today.

Why Has Heterogeneity of Iron-manganese Alloys Been Overlooked?

After the completion of the present investigation the question presented itself to the writer as to why the so obvious heterogeneity of iron-manganese alloys had not been recognized before. A more thorough study of original papers showed that, although the structures involved had been observed by many, their significance had not been understood.

Dr. Léon Guillet,¹⁶ whose work on special steels forms the basis of the classification of these steels, studied a series of low-carbon iron-manganese alloys (C - 0.12 per cent.), and observed many of the structures described

¹⁶ Léon Guillet: *Les Aciers Spéciaux*, p. 47 *et seq.* V. Ch. Dunod, Paris (1904).

by the author. He ascribed these structures, however, largely to carbon, described them in terms of cementite, martensite, etc. He noted that the pearlite had rather *une forme spéciale* but did not elucidate this any further. In the high-manganese alloys, obtained in the gamma condition, he observed the Widmanstättian structure, described by the writer for the 30 to 70 alloy, but referred to it as representing merely "cleavage planes."

It is of interest to note that Dr. Guillet refers to these cleavage planes as being analogous to those found in nickel steels. Why then not describe the Widmanstättian structure of meteorites—essentially iron-nickel alloys—also as cleavage planes? For the structure of meteorites is a faithful reproduction, on an enlarged scale, of the structure found in the polyhedra of "austenitic" nickel steels. A glance at the beautiful photograph of the structure of a meteorite given by Dr. Guertler¹⁷ will serve to establish this.

Following Guillet, a number of later investigators also describe the Widmanstättian structure of high-manganese steels as "cleavage planes."

Dr. H. M. Howe is of a somewhat different opinion. He devotes an entire chapter¹⁸ to "The Deformation Lines in Hadfield's Austenitic Manganese Steel," classifying them as "surface bands," "unheated etching bands," and "heated etching bands." The first ones are plain *slip* bands, according to Howe, the second "represent martensitization with the formation of beta iron caused by *slip*," while the third represent cementite precipitated along *slip* planes. In addition to these Dr. Howe finds suggestions of annealing twins, Neumann bands, X bands, amorphous iron and a "eutectiferous mass." On the whole it appears that Dr. Howe interpreted the lines in manganese steel to be deformation lines.

Dr. John A. Mathews,¹⁹ in accordance with Howe, refers to the Widmanstättian structure in manganese steel as "slip-lines." R. L. Dowdell and O. E. Harder follow his example in their recent paper on "The Decomposition of Austenite."²⁰ Dr. Hoyt describes the structure as "regular markings."²¹ Numerous other references of the same character could be cited.

Structures corresponding to those of the alloys Mn-2 and Mn-3 are universally described in terms of martensite, pearlite, cementite and ferrite.

¹⁷ W. Guertler: Metallographie, 1, Verlag von Gebrüder Borntraeger, plate 7. Berlin, 1912.

¹⁸ H. M. Howe: Metallography of Steel and Cast Iron, 1st ed., 460. McGraw-Hill Book Co., Inc. 1916.

¹⁹ John A. Mathews: Austenite and Austenitic Steels. *Trans.* (1925) 71, 568.

²⁰ R. L. Dowdell and O. E. Harder: *Trans. Am. Soc. Steel Treat.* (Feb., 1927) 12, 221.

²¹ S. L. Hoyt: *Op. cit.*, 339.

The importance of manganese as a creative influence, apart from the carbon, seems to have been realized first by Dr. J. O. Arnold and F. K. Knowles. In their "Preliminary Note on the Influence of Manganese on Iron,"²² they say:

Notwithstanding the supreme importance of the element manganese in iron and steel metallurgy, it is a curious scientific fact that the exact influence of nearly pure metallic manganese, alloyed in varying proportions, with nearly pure metallic iron is still unknown to steel metallurgists.

In a later paper, Arnold and Read²³ say ". . . The influence of the carbon is very considerable, but is by no means the dominating factor, which without doubt is the manganese." Arnold and Knowles²⁴ proved this contention by comparing the physical properties of two series of alloys in which the manganese varied from 1 to 20 per cent. In one of the series the carbon was about 0.85 per cent. while in the other "it was kept under 0.1 per cent." The description of Micrographic Features of Typical Nearly Carbonless Alloys is of interest in the present connection. The caption of the first photomicrograph reads:

Manganese 1.1 per cent. This consists of allotriomorphic crystals of manganiferous ferrite with dark etching *troostite* areas containing the double carbide of iron and manganese in an emulsified condition.

How "troostite" and "carbide" can be formed in notable quantities in "nearly carbonless" iron is surely mysterious, and no explanation is given of the caption of micrograph No. 2, which reads:

Manganese 4.1 per cent. This section exhibits a martensitic structure often well defined.

The caption of micrograph No. 4 is:

Manganese 19.85 per cent. This section exhibits the apparently *non-crystalline* and soft alloy, having the color of pale brass, which is typical of iron containing, say, from 15 to 35 per cent. manganese.

In their paper²⁵ Arnold and Read refer to the "white" constituent of alloys containing from 13 to 20 per cent. manganese as an "apparently amorphous substance." Clearly, Dr. Arnold failed to observe the Widmanstättian structure of high-manganese alloys.

Summarizing the evidence, it appears that although the principal structures of iron-manganese alloys were known to a number of earlier investigators, their correct interpretation, even in the case of Dr. Arnold,

²² J. O. Arnold and F. K. Knowles: Preliminary Note on the Influence of Manganese on Iron. *Jnl. Iron Steel Inst.* (1906) **69**, No. I, 106 *et seq.*

²³ J. O. Arnold and A. A. Read: The Chemical and Mechanical Relations of Iron, Manganese, and Carbon. *Jnl. Iron Steel Inst.* (1910) **81**, No. I, 172.

²⁴ J. O. Arnold and F. K. Knowles: The Mechanical Influence of Carbon on Alloys of Iron and Manganese. *Engineering* (Oct. 6, 1911) **92**, 478.

²⁵ J. O. Arnold and A. A. Read: *Op. cit.*

was hindered by ascribing undue importance to the small amounts of carbon present in the alloys. The great similarity of the iron-manganese structures to those of iron-carbon alloys was, without doubt, the main cause for their misinterpretation.

It is of interest to note, in this connection, that the structures of iron-nickel alloys have been misinterpreted in exactly the same manner, and this despite the fact that the system iron-nickel was shown by Osmond to be heterogeneous.

ACKNOWLEDGMENTS

The author wishes to acknowledge his indebtedness to his esteemed teacher, Prof. Albert Sauveur, in whose laboratory the present investigation was carried out, and to express his gratitude to E. L. Reed and C. H. Chou, of Harvard University, for valuable assistance.

SUMMARY

Structures exhibited by three typical alloys of pure iron and manganese, containing, respectively, 30, 8 and 3 per cent. manganese, are described and interpreted, attention being called to the fundamental meaning of the Widmanstättian and martensitic patterns in alloys, and to some aspects of photomicrography not generally understood.

It is shown that, contrary to universally accepted notions, alloys of iron and manganese are heterogeneous, consisting of several distinct constituents. The similarity of the iron-manganese structures to those of iron-carbon alloys is noted and its significance elucidated. The influence of carbon in imparting valuable properties to alloys of iron has been overemphasized, in the past, at the expense of that of other elements capable, by themselves, of yielding alloys with iron of remarkable properties.

In passing, attention is called to the misuse of the term "austenitic" in describing steels containing little, if any, austenite proper, and remedies are suggested to correct this.

Effect of Annealing on Cold-worked Single Crystals of Silicon-ferrite

By HUGH O'NEILL,* MANCHESTER, ENGLAND

(New York Meeting, February, 1928)

IN PREVIOUS papers,¹ the author has reported the results of experiments on the straining in tension of a single-crystal test piece, about 0.6 in. long, of vacuum-melted electrolytic iron containing 1.8 per cent. of silicon. The crystal was originally in the "as cast" condition, and was stressed slowly along a tetragonal axis so that slipping along conjugate gliding planes finally transformed the original cylindrical portion into a pair of fracture wedges. One of these fracture wedges was sectioned along the stress axis in a plane at right angles to the edge of the wedge. A metallographic study of this plane of section led to the conclusion that slip had taken place in the (111) direction along (112) planes making a V shape with the stress axis.

The present paper describes the results of scratch-hardness tests conducted on the same section, in order to determine the distribution of strain hardness therein, followed by annealing, and considers the resulting variations in hardness. These observations supplement those made by Krivobok² on similar material reduced 25 per cent. by hammering (*i. e.*, by impact) in the cold. In order to investigate ageing effects, two small crystals of the same alloy were also tested.

THE SPECIMENS EMPLOYED

The principal specimen, A, was prepared for the metallographic examination leading to the determination of the slip planes of the crystal. Therefore the work described in this paper was conducted on metal which had been repeatedly etched and had been allowed to rest for about 30 months after straining. It consisted of a section of the fracture wedge and contiguous unstrained head of the test piece taken along a tetragonal axis parallel to the direction of stressing, the plane of section *originally* being not far removed from the (011). Several subsequent grindings

* Lecturer in Metallurgy, University of Manchester.

¹ Hugh O'Neill: The Effect of Cold-work upon the Density of Crystals of α -Iron. *Jnl. Iron Steel Inst.* (1924) 109, 93; Deformation Lines in Large and Small Crystals of Ferrite. *Ibid.* (1926) 113, 417.

² V. N. Krivobok: A Photomicrographic Study of the Process of Recrystallization in Certain Cold-worked Metals. *A. I. M. E. Pamphlet No. 1557-E* (1926).

and polishings may have altered slightly the orientation of this surface from that originally determined, but successive series of hardness tests were conducted on planes as nearly parallel to each other as careful hand polishing permits. Their absolute orientation will not be given more definitely.

The other crystals used, B and C, were much smaller in size and were chosen from the same batch of metal.

SUITABLE HARDNESS TESTS FOR SINGLE CRYSTALS

The Brinell test is not ideal for studying hardness effects in single crystals, because, although the ball impressions remain spherical (or spheroidal) the surface of the crystal piles up in certain directions around the indenter and produces "lobes" or "pressure figures," which render a true measurement of the area of contact difficult to determine. The error from this cause is not necessarily great if an average is made of several diameter readings.

The Rockwell machine has the advantage of employing only depth measurements, but the system is empirical and does not take into account the variable upward extrusion of the metal which is the cause of "lobe" formation. Some Rockwell results are reported in Table 8, which show that the test is sensitive to strain-hardening effects in single crystals.

The Herbert "Pendulum" instrument does not require the measurement of indentation diameters, and is therefore quite suitable for crystal work. A random face of an iron crystal with 1.8 per cent. silicon gave a "time hardness" of 21.0, which after cold-rolling rose to 33.0.

The scratch test is attractive from many points of view, but Tammann quotes results³ showing that cold working is without effect upon the scratch hardness of metals. Why this should be so is not clear, and in connection with work undertaken for the Carnegie Scholarship of the Iron and Steel Institute a scratch instrument has been constructed and fully tested, of which detailed particulars will appear elsewhere.⁴ Using a spherical diamond tool 1 mm. in diameter under various loads, very satisfactory results have been obtained which clearly make evident the effect of cold work in metals.

This instrument was applied to the crystal specimens under examination, and proved highly satisfactory. With a load of 500 gm., the edges of the scratches were very well defined, owing to the absence of grain

³ F. Körber and P. J. H. Wieland: Ueber Kaltwalzen und Ausglühen von Kupfer-Zink-Legierungen. *Mitt. d. Kaiser-Wilhelm, Inst. f. Eisenforschung, Dusseldorf* (1921) 3, 57; O. Faust and G. Tammann: Eine Methode zur Bestimmung der untern und oberen Elastizitätsgrenze usw. *Ztsch. phys. chem.* (1911) 75, 123.

⁴ Hardness and Its Relation to the Cold-working and Machining Properties of Metals. *Carnegie Schol. Mem.*, Iron and Steel Inst. (1928) 17, 109.

boundaries and varied orientations, and scratch widths were measured with accuracy on a metallurgical microscope ($\frac{1}{5}$ in. objective) with a graduated eyepiece. The eyepiece was calibrated repeatedly against a standard engine-divided millimeter scale. The specimen to be tested was mounted in plasticine on a base plate, leveled and set up on the inclined mechanical stage of the sclerometer. A microscope with cross hairs, mounted on the sclerometer, made it possible to rule scratches in any direction, for by using some line on the specimen as a datum the cross hairs could be rotated through a given angle against a protractor scale and the base plate adjusted on the table until the datum line again coincided with the cross hair. This sclerometer microscope also allowed scratches to be made through any chosen spot of a specimen.

After the scratches had been ruled, the base plate and specimen were transferred to the mechanical stage of the measuring microscope and the scratch widths (w) were read at regular intervals along their lengths. The location of the scratches with respect to the edges of any specimen was determined by readings in two dimensions of this mechanical stage. Hence the strain-hardness distribution may be determined and "isosclers" may be plotted on a diagram. Considering this process of scratching as the steady pressing of a spherical tool against the specimen so that the latter is caused to flow to each side of the bearing surface, a scratch-hardness value will be given by load on tool horizontal projected area of contact surface:

$$H_s = \frac{L}{\frac{1}{2} \cdot \frac{\pi}{4} w^2} = \frac{SL}{\pi w^2}$$

SCRATCH TESTS ON SECTIONED FRACTURE WEDGE

The crystal fracture wedge described was set in Rose's metal and given a careful metallographic polish. It was etched for 15 min. in 4 per cent. alcoholic nitric acid to remove flowed surface metal and was then given a final light polish to insure well defined sclerometer scratches. It was set up so that scratches could be ruled under a load of 500 gm. at right angles to the top edge of the test piece; i. e., along the tetragonal and stress axis. As it was feared that the later annealing experiments might cause interfering recrystallization features below the sclerometer scratches, the number of these was kept at a minimum in order to leave as much surface as possible unimpaired for subsequent tests. The aim was to have one scratch near the axis of the specimen and one on each side of that axis, the scratches to start in the unstrained head of the test piece and to cross the edges of the wedge.

After measurement of the first series of scratches reported in Table 1, the specimen was etched to display the deformation markings or "etch

bands" described in a previous paper.⁵ It was found that the etch bands were associated with fairly sharp changes of strain hardness, though regions free from pronounced etch bands nevertheless gave scratch widths indicative of hardening effects. From the results reported in Table 1, Fig. 1 has been constructed.

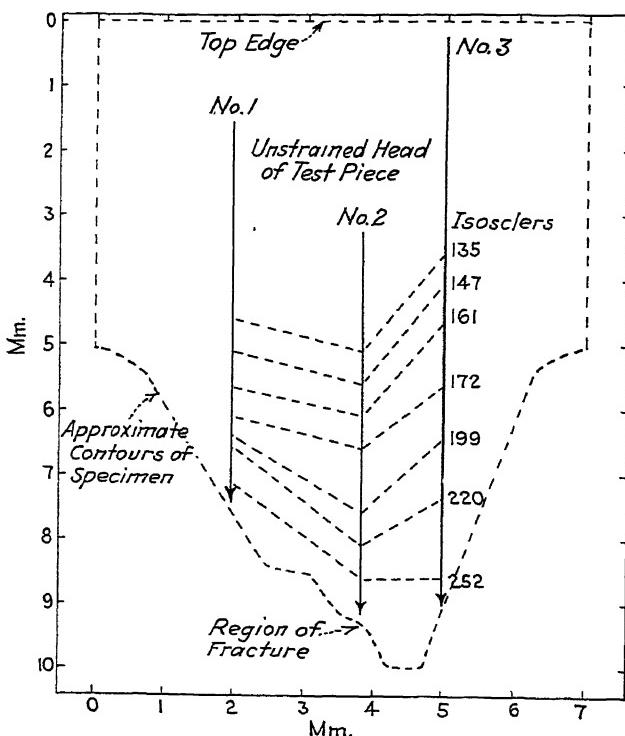


FIG. 1.—SCRATCH TESTS ON SECTIONED FRACTURE WEDGE.

Scratches made well to the left-hand side of the axis of the specimen ran through a region free from pronounced etch bands and always decreased steadily in width from the head to the edge of the wedge. The other scratches frequently showed sudden jumps in hardness values, and these must be associated with the etch band regions which they traversed. The general V form of the isosclers suggests a hardening of the crystal along the crystal slip planes, confirming generally the current ideas of wedge production as developed, for instance, by Goucher.⁶

⁵ Hugh O'Neill: *Jnl. Iron Steel Inst.* (1926) **113**, 417.

⁶ F. S. Goucher Studies on the Deformation of Tungsten Single Crystals under Tensile Stress. *Phil. Mag.* (1924) **48**, 800.

TABLE 1.—*Scratch Tests on Sectioned Fracture Wedge "A"*

Distance from Top Edge, Millimeters	Scratch Width (in), Millimeters		
	No. 1	No. 2	No. 3
0.6			0.096
1.1			0.096
1.6			0.097
2.1	0.097		0.096
2.6	0.095		0.097
3.1	0.097		0.097
3.6	0.097	0.103	0.097
4.1	0.097	0.101	0.091
4.6	0.097	0.097	0.089
5.1	0.093	0.097	0.086
5.6	0.091	0.093	0.086
6.1	0.086	0.089	0.084
6.8	Etch band		
6.4	0.080		
6.6	0.073	0.086	0.078 Etch band
7.1	0.071	0.086	0.079
7.3		Etch band	
7.6		0.080	0.074
8.1		0.076	0.073 Etch band
8.6		0.071	0.071
9.0			0.071
Distance from axis of specimen, mm.....	-1.6	+0.3	+1.5
Maximum width.....	0.097	0.103	0.097
Minimum width.....	0.071	0.071	0.071

FIRST ANNEALING OF SPECIMEN A

The specimen was carefully melted from its Rose's metal setting and heated *in vacuo* in an electric furnace. After 40 min. the thermocouple indicated 605° C. and this temperature was maintained for 15 min. After cooling in the furnace, the specimen was carefully given a very light polish direct on the pad and retested on the sclerometer. The results given in Table 2 show that softening had commenced.

The specimen was etched for about 15 min. and carefully examined, but no signs of recrystallization could be detected. No new grains were found even on the sites of scratches 1, 2 and 3. Some of the streak markings seemed more prominent and roughened, and this alteration of etching properties may indicate the initiation of grain formation,

TABLE 2.—*Scratch Tests after Annealing at 605° C.*

Distance from Top Edge, Millimeters	Scratch Width, Millimeters	
	No. 4	No. 5
4.2		0.097
4.7		0.096
5.2	0.097	0.097
5.7	0.097	0.097
6.2	0.094	0.093
6.7	0.093	0.091
7.2	0.089	0.089
7.7	0.084	0.086
8.2	0.084	0.083
Distance from axis of specimen, mm.....	-0.3	+0.2
Maximum width.....	0.097	0.097
Minimum width.....	0.084	0.083

SECOND ANNEALING OF SPECIMEN A—SURFACE FLOW

The specimen was again heated *in vacuo* in a furnace in which the temperature rose to 740° C. in 30 min. It was maintained at this temperature for an additional 30 min. and then cooled in the air. After setting in Rose's metal, the test piece was rubbed down on coarse emery cloth to remove previous etch markings and finally was given a rather drastic polishing on the pad. Scratches 6 and 7 were then made in opposite directions, and the measuring microscope showed that their edges were finely and regularly serrated. Running from the serrations into the surrounding metal were very fine straight lines, pointing in the direction along which the diamond had moved. The effect suggested that the scratching tool had "pulled" the surface with it, and the measurements showed that the unstrained head of the crystal gave somewhat narrower scratches than it did before this last annealing. Hardening due to the Beilby surface flow during polishing was suspected, so the specimen was lightly etched before making scratch No. 8. The results given in Table 3 show that etching had removed a hard layer which caused a reduction in scratch width of something like 2 or 3 per cent. The general softening proceeded and the etch bands continued to be localities of maximum strain hardness.

Many tests were made to check the reliability of the sclerometer, particularly to guard against decrease in the scratch width on account of faulty design. Confirmation of the latter point is afforded by scratch 7, which was made in the reverse direction but gives a similar result.

TABLE 3.—*Specimen A after First Annealing at 740° C.*

Distance from Top Edge, Millimeters	Scratch Width (<i>w</i>), Millimeters		
	No. 6*	No. 8*	No. 7*
2.1			0.095
2.6	0.094		0.095
3.1	0.095		0.097
3.6	0.095	0.099	0.097
4.1	0.095	0.099	0.097
4.6	0.095	0.099	0.097
5.1	0.096	0.097	0.095
5.6	0.095	0.097	0.095
6.1	0.095	0.097	0.095
6.2			Etch band
6.6	0.095	0.095	0.091
7.1	0.091	0.093	0.086
7.6	0.089	0.086 Etch band	
8.1		0.089	
8.6		0.086	
Distance from axis of specimen, mm.....	-1.1	+0.4	+2.1
Maximum width.....	0.096	0.099	0.097
Minimum width.....	0.089	0.086	0.086

* Scratches 6 and 7 were made on a highly polished and unetched surface. Scratch 8 was made after light etching.

THE FIRST RECRYSTALLIZED GRAINS

In order to secure a better metallographic preparation the specimen was repolished, and carefully re-etched. By thorough examination, two points were discovered within the etch bands at which recrystallization had commenced. The specimen was accurately measured up on the mechanical stage and the position of the two new crystal grains was determined (see Fig. 2).

Photomicrographs at 200 diameters were taken of each center of recrystallization (Figs. 3 and 4). The new grains are intimately associated with the etch band markings: in fact, they form from the latter and have a major axis lying in the same direction as that of the etch bands. Scratch 8 just avoided the new grains, and the reading at 7.6 mm. shows the existence of an etch band and a concentration of hardness. Each end of that very band connected with the new grains α and β indicating that the highly strain-hardened regions of a deformed crystal correspond with the commencement of recrystallization in those regions. The straight boundaries noticeable in the new grains suggest that such boundaries are related to the traces of previous crystal slip.

At the left-hand side of the apex of the wedge, some indistinct markings were observed, near the cubic fissures, which were probably fine new recrystallized grains.

To investigate whether time as well as temperature played a part in recrystallization, the setting was melted from the specimen and the latter was again reheated *in vacuo*. After 45 min. in the furnace the temperature had risen to the previous value of 740° C., and it was maintained

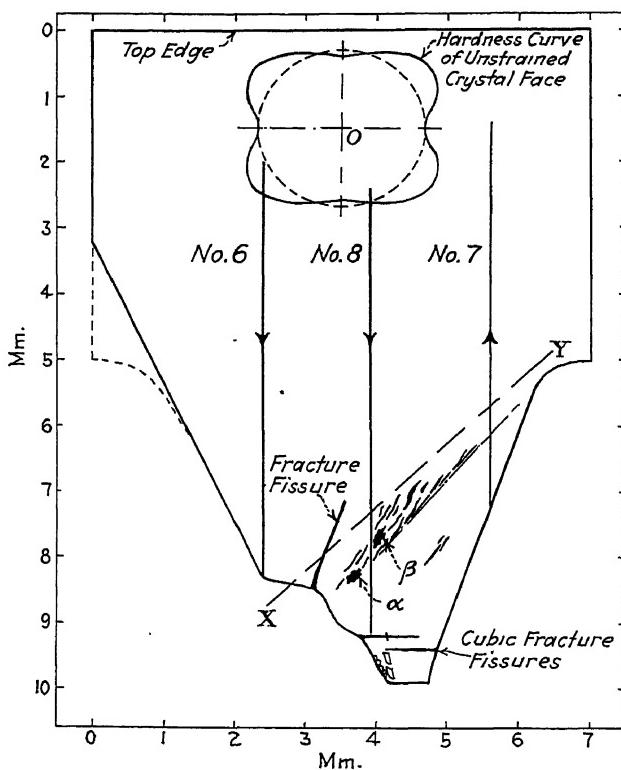


FIG. 2.—TWO NEW GRAINS, α AND β , WITHIN ETCH BAND AFTER FIRST ANNEALING OF SPECIMEN AT 740° C.

there for 2 hr. After polishing on the pad, the specimen was given a fairly deep etch and examined under the microscope.

The regions previously shown in Figs. 3 and 4 were again photographed and are reproduced as Figs. 5 and 6. It is clear that as the period of annealing at 740° C. was lengthened, both recrystallization and grain growth proceeded. The grain shown in Fig. 3 occupies the same position as the much larger grain at the bottom of the group of crystals in Fig. 5. In Fig. 6, the transformation of streaky etch bands into new grains is clear. Tiny crystals had commenced to form round certain non-metallic inclu-



FIGS. 3 AND 4.—THE TWO CENTERS OF RECRYSTALLIZATION, α AND β . $\times 200$.

FIGS. 5 AND 6.—SAME AS FIGS. 3 AND 4 AFTER REHEATING IN VACUO AND SUBJECTION FOR 2 HR. TO A HEAT OF 740° C. $\times 100$.

(Reduced to $\frac{4}{5}$ original scale, original magnification given.)

sions. Such inclusions generally cause concentrations of stress during deformation.

The specimen was set up on the sclerometer so that scratches might be drawn through the recrystallized regions. The results are given

TABLE 4.—*Specimen A after Second Annealing at 740° C.*

Distance from Top Edge, Millimeters	Scratch Widths (<i>w</i>), Millimeters			
	No. 9	No. 12	No. 11	No. 10
2.1	0.105		0.108	
2.6	0.105			0.109
3.1	0.104	0.106	0.106	0.109
3.6	0.103	0.106	0.106	0.109
4.1	0.103		0.105	0.108
4.6	0.101	0.104	0.104	0.107
5.1	0.101			0.105
5.6	0.101	0.107	0.103	0.105
6.1	0.101	0.104	0.104	0.105
6.3	0.099			
6.6		0.101	0.101	0.103
7.1		0.101	0.093	0.101
7.6		0.095	0.095*	Etch band region
7.8		0.101*(Ragged)		
7.9		0.101*(Ragged)		
8.1		0.095	0.095	
8.6		0.098	0.098	
9.1		0.097	0.098	
9.3			0.095	
Distance from axis of specimen, mm.....	-1.8	+0.7	+1.1	+2.0
Maximum width.....	0.105	0.107	0.108	0.109
Minimum width.....	0.099	0.095	0.093	0.099

*Recrystallized area.....

0.101

0.095

in Table 4. It appears from the readings at 7.1, 7.6 and 7.8 mm. that the soft new grains occur in the regions which are still the hardest parts of the specimen. Furthermore, the new grains give a higher scratch-hardness result than the undeformed head of the test piece, as though the metal surrounding them was restricting their tendency to be fully softened. The readings in the unstrained head indicate a softening of the crystal from the "as-cast" condition as a result of annealing. It is true that the thorough etching treatment given in this case may account for some of the broadening of the scratches as compared with those made in previous tests, but the author is confident that a real softening can be detected. Solidification stresses entail the natal production of com-

paratively imperfect crystals of metals. Annealing dissipates such internal stresses and allows the "blocks" which may be considered to form the "mosaic" of the imperfect crystals⁷ to be pulled into line, thus giving a more uniform lattice structure. A sharpening of X-ray reflection spots, a lowering of elastic limit, and a decrease in hardness result from this process.

ANISOTROPY OF A METALLIC CRYSTAL

The mechanical properties of single crystals differ in different directions, and scratches made in different directions on a given crystallographic plane may indicate varying hardnesses. This effect was tested in the head of the present crystal by making pairs of scratches at various inclinations to the top straight edge of the specimen. The sclerometer microscope was used for setting up the crystal each time on the sclerometer stage, and 10 readings of width were made for each scratch and averaged. The results appear in Table 5.

TABLE 5.—*Directional Hardness of Crystal A*

Angle Made by Scratch with Top Edge of Crystal	Scratch Width (w), Millimeters	H_{B} , Kg. per Sq. Mm.
90° (001) trace.....	0.108	110
180° (010) trace.....	0.104	118
55° (111) trace (?).....	0.096	138
35° (112) trace (?).....	0.091	154

Mineralogists generally find that the scratch hardness of minerals is least in a direction parallel to the traces of cleavage planes. It has previously been shown by the author that X-ray reflections from a cleavage face of iron indicate cubic cleavage. It is interesting therefore to observe that the scratch hardness of this metallic crystal was lowest in a direction parallel to cubic (001) traces. The results are shown diagrammatically at the top of Fig. 2, the distance from the point O along any direction being the hardness value of the metallic crystal in that direction. For an isotropic material the hardness curve would be a circle.

FOURTH AND FIFTH ANNEALINGS OF SPECIMEN A

The specimen was again heated *in vacuo* and had reached 825° C. in 90 min. It was allowed to cool and after polishing showed that recrystallization had progressed at the apex of the wedge. The two areas shown in Figs. 5 and 6 had merged, giving a recrystallized band across the specimen in the direction XY (Fig. 2).

⁷ W. L. Bragg, C. G. Darwin and R. W. James: The Intensity of Reflexion of X-Rays by Crystals. *Phil. Mag.* [7] (1926) 1, 905.

The fifth annealing consisted of raising the temperature to 850° C. in 1 hr. and maintaining it there for 40 min. Etch bands were no longer visible in the polished and etched specimen, and the part of the wedge below the line XY consisted entirely of large recrystallized grains. A large new grain was also forming on the left of the curved fissure and tending to grow to the left; the only recrystallization yet apparent in the left-hand portion of the wedge. Scratch results are given in Table 6.

TABLE 6.—*Specimen A after Annealing at 850° C.*

Distance from Top Edge, Millimeters	Scratch Widths, Millimeters		
	No. 13	No. 14	No. 15
2.9			0.100
3.9			0.101
4.4		0.100	0.101
4.9	0.098	0.099	0.098
5.9	0.099	0.099	
6.4	0.098	0.099	
6.9	0.096	0.097 { Just before entering new grain	0.095 { Just before entering new grain
7.2	0.095	0.093 Grain No. 1	0.0955 Grain A
7.4	0.094	0.095 Grain No. 2	
7.6	0.093	0.093 Grain No. 3	0.098 Grain B
8.1		0.094 Grain No. 4	0.099 Grain C
9.1		0.095 Grain No. 6	
9.3		0.096 No grain visible	
Distance from axis of specimen.....	-1.6	+0.1	+1.6

The scratch widths varied from grain to grain in the recrystallized areas, and here the scratches presented a somewhat ragged appearance. Differences in surface level due to etching did not make it possible to decide whether grain boundaries caused any hardening effect. The widths for the unstrained head are somewhat smaller in these tests than in those given in Table 4, and in this region the scratches were festooned with faint slip bands. After etching for 2 min. more, some check tests were made, and the unstrained head gave readings averaging 0.104 mm.

It is noteworthy that above the line XY no new grains have appeared. Apparently the deformation in this region was not sufficient to initiate grain production. At certain places the appearance of the polishing scratches suggested that the orientation of the metal was not uniform, though etching betrayed no sharp crystal boundary. After careful search two places were found in this region where deep etching revealed a faint marking resembling an embryonic boundary. One of these mark-

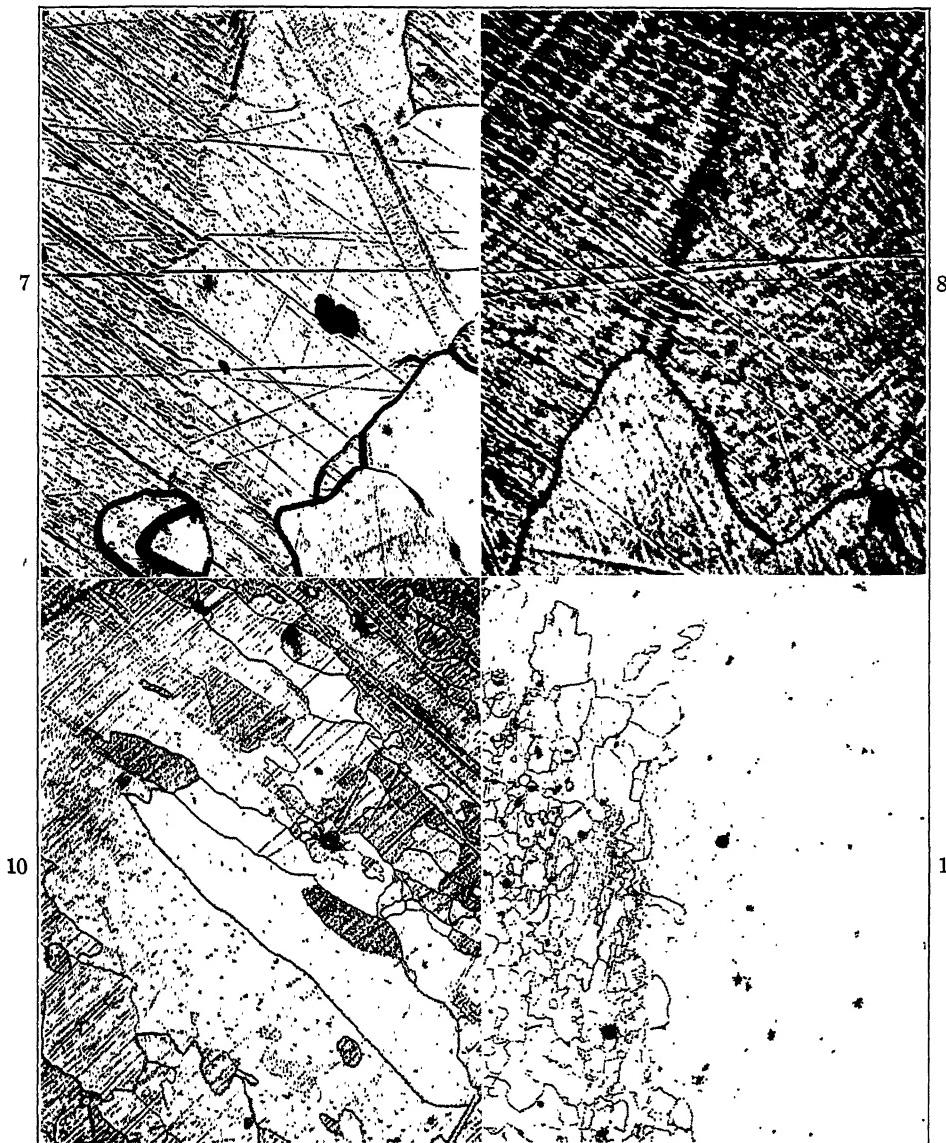


FIG. 7.—EMBRYONIC BOUNDARY DISCERNED ABOVE LINE XY OF FIG. 2. COMPARE WITH BORDER OF ADJACENT RECRYSTALLIZED METAL. $\times 140$.

FIG. 8.—SECOND EMBRYONIC BOUNDARY IN REGION OF FIG. 7, BROUGHT INTO VIEW BY ROTATING THE VERTICAL ILLUMINATOR AND PUTTING THE SPECIMEN JUST OUT OF FOCUS. $\times 140$.

FIG. 10.—RECRYSTALLIZATION NOTED AFTER LAST ANNEALING OF CRYSTAL B. $\times 140$.

FIG. 11.—CHANGE FROM STRUCTURELESS REGION TO THAT OF FINE AGGREGATE IN RECRYSTALLIZED SPECIMEN B. $\times 140$.

(Reduced to $\frac{1}{3}$ original scale, original magnification given.)

ings can be seen in Fig. 7, and may be compared with the borders of the adjacent recrystallized metal. (The kinking of the polishing scratches will help in its location, the inclined marking on the right being the remains of a sclerometer scratch.) Here it seems that we are reaching the limit of sensitiveness of chemical etching for displaying grain boundaries, or it may be that there is very little difference in orientation on opposite sides of this undeveloped dividing line. The specimen was examined under concentric oblique illumination, and was rotated through 180°,

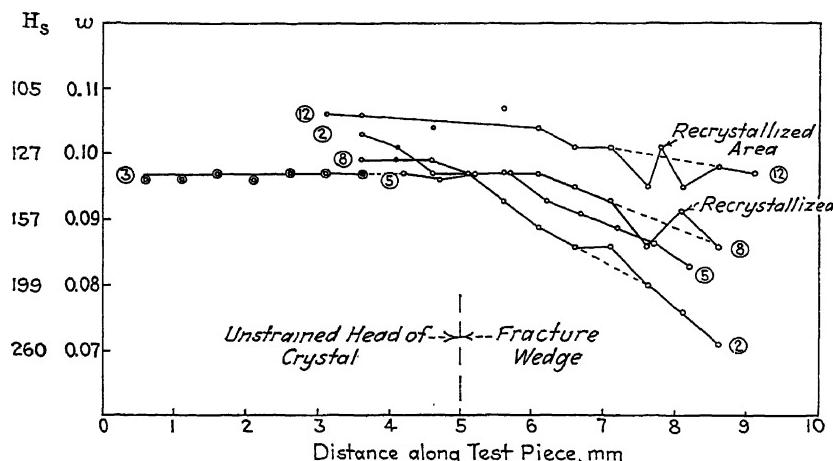


FIG. 9.—SCRATCH TESTS NEAR AXIS OF CRYSTAL A, AFTER VARIOUS ANNEALINGS.

but did not give the effect usually associated with boundaries. In Fig. 8 the vertical illuminator was rotated to give a darkening effect, and the specimen was brought just out of focus, enabling the second embryonic boundary to be distinguished.

TABLE 7.—*Fracture Wedge A*

Treatment	Date	Scratch Width, Millimeters	Scratch Hard- ness, Kg. per Sq. Mm.
Strained in tension to fracture.	May 1, 1924		
Section scratched.....	Oct. 10, 1926		
"As-cast" head.....	Oct. 10, 1926	0.097	136
Region of fracture.....	Oct. 10, 1926	0.071	252
Heated at 600° C. 15 min..	Oct. 16, 1926	0.083	185
Heated at 740° C. 30 min..	Oct. 19, 1926	0.088	163
Heated at 740° C. 2 hr....	Jan. 4, 1927	0.093 0.100	147
		Recrystallized grains	
Heated at 825°-850°.....	Jan. 14, 1927	0.095 ±	141
Annealed head.....	Jan. 14, 1927	0.104	118

Certain results of specimen A are tabulated in Table 7, and the widths of the scratches made near the axis of the specimen after each annealing treatment are plotted in Fig. 9.

LOW-TEMPERATURE ANNEALINGS OF DEFORMED CRYSTALS

Heating below the recrystallization temperature frequently causes a slight increase in the hardness of cold-worked metals. To study this effect in single crystals, two further specimens were examined. Crystal B had been cold-rolled about 20 months earlier and tested at intermediate stages of rolling with the Rockwell hardness machine. After the last rolling the "pressure figures" given by the test were squarish in appearance. After polishing and etching, a clear portion (*P*, Fig. 12) of the streaky surface (*Q*, Fig. 12) was chosen for scratch tests, which were con-

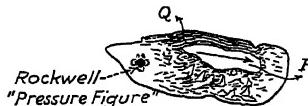


FIG. 12.—CRYSTAL B AFTER ROLLING AND ETCHING.

ducted in parallel pairs after suitable heat treatments of 30 min. duration followed by polishing and etching for 1 min. The results are given in Table 8. After the last annealing, recrystallization had set in, area *Q*

TABLE 8.—*Crystal B, Aged*

Treatment	Date	Scratch Width, mm.	Scratch Hardness <i>H</i> _s
As cast.....	May 22, 1925	Rockwell (60 kg.)	
		47.2	
Cold-rolled 24% r. t.	May 22, 1925	56.0	
Cold-rolled 67% r. t.	May 22, 1925	61.4	
Cold-rolled 80% r. t.	May 22, 1925	61.3	
<hr/>			
Scraped after standing at room temp.....	Jan. 11, 1927	0.0755 mm.	224
Heated 250° C. for 30 min.....	Jan. 12, 1927	0.0761	220
Heated 350° C. for 30 min.....	Jan. 12, 1927	0.0766	216
Heated 450° C. for 30 min.....	Jan. 17, 1927	0.0830	185
Heated 600° C. for 30 min.....	Jan. 19, 1927		
(a) same area.....		0.0882 }	163 }
(b) recrystallized area.....		0.093 }	147 }

for instance, consisting of fine grains mixed with long straight-sided grains which had obviously formed from etch bands (Fig. 10). Area *P* changed suddenly from a structureless region to that of the fine aggregate at the adjacent edge of area *Q* (Fig. 11).

The second specimen, crystal C, was prepared and tested on the sclerometer, cold-rolled, polished, etched and retested. The scratches

were completed about 30 min. after rolling, and the first heat treatment commenced 2 hr. after rolling. The scratches on the rolled crystal were somewhat ragged, as though they were passing through regions of slightly variable hardness. With the intention of securing greater regularity where etching had caused variations in level, a light polish was given. The Beilby layer was at once detected, as the scratch widths dropped from 0.0766 mm. to 0.0735 mm. The annealings at 450° C. and 600° C. for both specimens B and C were made in the bath together, and the results for the latter are given in Table 9.

TABLE 9.—*Crystal C*

Treatment	Date	Scratch Width, mm.	Scratch Hardness H_s
As cast.....	Jan. 15, 1927	0.0950	141
Cold-rolled 70% red. thick. scratched 30 min. later.....	Jan. 15, 1927	0.0766	216
Heated 250° C. for 30 min.....	Jan. 15, 1927	0.0788	205
Heated 450° C. for 30 min.....	Jan. 17, 1927	0.0830	185
Heated 600° C. for 30 min.....	Jan. 19, 1927	0.0975	134
		d	H
Brinell hardness of recrystallized specimen 1 mm. ball, 30 kg.....	Jan. 24, 1927	0.506	139

After heating at 600° C., specimen C has recrystallized completely, but it may be noted that it is not as soft as the annealed unicrystalline portion of specimen A, though softer than in its own original as-cast condition. The hardness results for both B and C are plotted in Fig. 13.

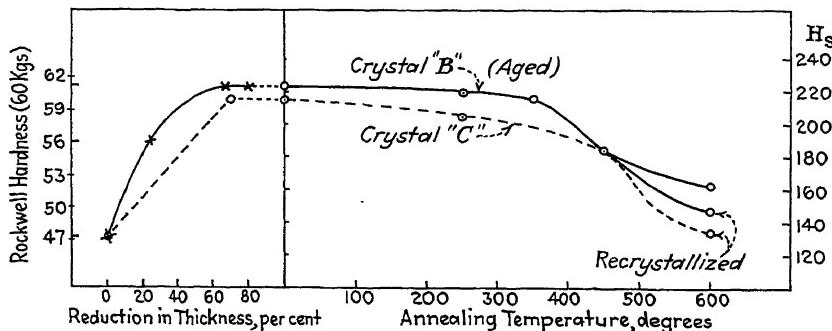


FIG. 13.—GRAPH OF HARDNESS RESULTS OF CRYSTALS B AND C.

In neither case can low-temperature hardening be noticed, though the specimens have had similar amounts of deformation. The effect of ageing these rolled crystals by allowing them to stand for many months is clearly to inhibit subsequent softening and recrystallization. The

recrystallized area of specimen B, for example, is not as soft as that of specimen C although the former has had an extra annealing treatment.

Brinell tests with the 1-mm. ball were made on recrystallized specimen C, and the similarity in value between the standard Brinell number and the scratch-hardness number will be noticed. The ball indentations indicated a "preferred orientation" in the recrystallized metal, as they were surrounded by four lobes making right-angled crosses.

DISCUSSION OF THE RESULTS

The plastic deformation of metals is known to take place by gliding along slip planes with the production generally of surface slip bands. Thompson and Millington's⁸ explanation of the genesis of slip bands differs from the original "block slip" theory by supposing that any one band is made up of several moved atomic layers, and this explanation has been approved by Dr. Rosenhain. The traces of the effects of this gliding are sometimes found beneath the exposed surfaces of metals when the crystals are polished and etched after sectioning. Etch bands are then frequently seen in both deformed aggregates and single crystals, and they would appear to represent internally the regions of moved layers which give rise to the external slip bands. The work described in this paper shows that in a setting of parent metal which is itself strain-hardened they are especially hard and are the seats of initial recrystallization.

It appears that there is a similarity between the etch band regions in deformed single crystals and the grain boundaries in deformed aggregates, for (1) both are regions of strength, and (2) both are the primary regions of recrystallization.⁹ As there must be special atomic conditions at grain boundaries, so there may be similar atomic conditions on the used glide planes and etch bands, or at least conditions giving similar effects. It has previously been pointed out by the author¹⁰ that gliding in α -iron crystals in the (111) direction along (112) planes may lead to the production of twinned layers. The etch bands may therefore contain twinned lamellae. In this connection, Carpenter and Elam have shown that twin boundaries are the seats of recrystallization.¹¹ Otherwise, if etch bands be looked upon as resembling ribs composed of very

⁸ F. C. Thompson and W. E. W. Millington: The Plastic Deformation of α - and γ -iron. *Jnl. Iron Steel Inst.* (1924) **109**, 67.

⁹ H. C. H. Carpenter and C. F. Elam: Stages in the Recrystallization of Aluminum Sheet on Heating: With a Note on the Birth of Crystals in Strained Metals and Alloys. *Jnl. Inst. Metals* (1921, I) 259; F. Adcock: The Internal Mechanism of Cold-work and Recrystallization in Cupro-nickel. *Ibid.* (1922, I) 73; C. H. Mathewson and A. Phillips: Recrystallization of Cold-worked Alpha Brass on Annealing. *Trans. (1916)* **54**, 608.

¹⁰ Hugh O'Neill: *Jnl. Iron Steel Inst.* (1924) **109**, 93. *Op. cit.*

¹¹ See reference No. 9.

minute crystals, their especial hardness could be compared with the recognized hardness of microcrystalline aggregates. At the same time, that they are the seats of recrystallization could also be ascribed to the corresponding causes existing at grain boundaries, whatever those causes may be. So far neither phenomenon is properly understood, but the explanation of the one would probably fit the other.

Generally speaking, the effect of increasing the specimen's mean atomic amplitude by raising the temperature during annealing will be to enable the atoms to return to a normal undeformed lattice. Annealing a cold-worked crystal would therefore appear to initiate softening at any (raised) temperature. The evidence in this paper shows that a deformed single crystal of ferrite commences to soften at comparatively low annealing temperatures, and before any new grains appear which can be recognized microscopically. Furthermore, no "temper-hardening" was observed, and this agrees with the generalization just made concerning annealing. Yet temper-hardening is known to occur in many cases during the heat treatment of deformed aggregates. It is not always found, and the reasons for its occurrence are not clear. Angus and Summers¹² observed it during the annealing of deformed copper which originally was comparatively coarse grained, but the finer grained material softened continuously on heating. Pilling and Halliwell¹³ could not find it in copper aggregates, and while Matsuda¹⁴ noticed the effect in α -brass, aluminum-bronze and phosphor bronze it was absent in seven other metals examined. It may be that it is a difference effect between the general softening of the mass and the tendency to hardening by the production of a shower of ultramicroscopic grains round the old grain boundaries as recrystallization is initiated. Such grains grow larger as annealing proceeds, and this hardening associated with microcrystallinity therefore decreases. If the minute grains are produced and provide a stiffening effect before the general softening has set in sufficiently, the net result is a hardening. Further annealing, however, will cause a net softening by the dual process of growth of the minute grains and the progressive removal of strain hardening.

The effect of prolonged rest after deformation in delaying recrystallization and softening has been noticed also by Krivobok.¹⁵ If during the early stages of annealing, competing hardening and softening influences

¹² H. T. Angus and P. F. Summers: The Effect of Grain-size upon Hardness and Annealing Temperature. *Jnl. Inst. Metals* (1925, I) 115.

¹³ N. B. Pilling and G. P. Halliwell: Softening of Hard-rolled Electrolytic Copper. *Proc. Am. Soc. Test. Mat.* (1925) **25**, 97.

¹⁴ T. Matsuda: The Effect of Cold-working and Annealing on Some Physical Properties of Copper, Aluminum and their Alloys. *Sci. Repts. Tokoku Imperial Univ. [1]* (1925) **14**, 343.

¹⁵ V. N. Krivobok: *Op. cit.*

are at work, as suggested above, the delay in softening may be ascribed to an extension of the annealing range over which these two effects practically neutralize each other. If aging facilitates the initiation of recrystallization at many centers as opposed, in its absence, to fuller development of new grains at fewer centers, the hardening effect would be more prolonged. Recrystallization would also not be apparent so early, as the grains would not have grown to sizes readily recognizable under the microscope. Much more work is required, however, before the question can be settled.

Summary

(1) Subcutaneous deformation markings are revealed on etching polished sections of slowly cold-worked single crystals of silicon-ferrite. Scratch tests indicate the concentration of strain hardness at these etch bands and also the increase of strain hardening from the base to the line of fracture of a sectioned crystal "fracture wedge."

(2) Annealing these cold-rolled single crystals at 250° C. either shortly after rolling or after a rest of 20 months gave no measurable rise of scratch hardness. With such a heat treatment a hardening effect might have been expected; if anything a slight softening was indicated. Heating at higher temperatures caused pronounced softening of a crystal fracture wedge before any sign of metallographic recrystallization could be detected.

(3) Incipient recrystallization was observed at two points in the main "etch band" system after heating a certain crystal fracture wedge at 740° C. for 30 min. Recrystallization and softening was then progressive in the sense that the use of (a) longer periods of annealing at a given temperature, or (b) higher temperatures, caused further general softening and the appearance of more new grains, together with some growth of previously existing grains. After these annealing treatments no recrystallization was apparent in the less distorted basal portions of the fracture wedge.

(4) Generally speaking, a major axis of the new grains followed the direction of the "etch bands." The soft recrystallized grains were generally surrounded by relatively severely strain-hardened metal, and their scratch hardness was higher than that of the annealed unstrained head of the crystalline test piece. This suggests that the new grains are still subjected to some hardening strains.

(5) The effect of a long time interval between deformation and heat treatment is to retard both softening and recrystallization.

(6) Scratch tests have demonstrated: (a) that a hard surface layer can be produced on metallic crystals by polishing, and that this layer can be removed by etching; (b) that annealing a metallic crystal in the "as cast" condition causes it to soften; (c) that the hardness varies in dif-

ferent directions along a given crystallographic face, and appears to be least in the direction parallel to the traces of (001) planes.

ACKNOWLEDGMENTS

The author is indebted to Dr. M. L. Becker, for assistance with the annealings, and to Prof. F. C. Thompson, for providing facilities for carrying out this work and for kindly interest.

DISCUSSION

S. L. HOYT, Schenectady, N. Y.—Mr. O'Neill called attention to the hardness of cold deformed metals as compared to the hardness of annealed metals as determined by the scratch test. In the literature, as Mr. O'Neill points out, we read that the two conditions of the metal have the same scratch hardness, and yet Mr. O'Neill shows that, in his own work, the cold deformed metals have a higher scratch hardness. It seems to me that we have left that point hanging fire about long enough, and the main object of my discussion is to suggest that somebody, possibly the Bureau of Standards, go into that question and let us have a rather thorough analysis of the scratch hardness of annealed and cold-worked metals.

From the work that was presented here by Mr. Schermerhorn and myself, two years ago, it is evident that a metal may show the same hardness in the annealed state that it will in the cold deformed state. That is brought about by properly selecting the conditions under which the test is made.

Mr. O'Neill used a diamond ball for determining the scratch hardness, while the Martin's thermometer uses a diamond point. These conditions differ so much that possibly in that circumstance we find the correct interpretation of the different results observed.

H. O'NEILL (written discussion).—The point raised by Dr. Hoyt has interested me for some time and since the paper under discussion was written I have made a large number of scratch tests on various metallic specimens. The results—together with a full description of the sclerometer—are now available in the Carnegie Scholarship Memoirs,¹⁶ and convince me that, speaking generally, the scratch test does indicate increased hardness in cold-worked metals.

¹⁶ H. O'Neill: Hardness and Its Relation to the Cold-working and Machining Properties of Metals—Part II. *Carnegie Schol. Mem.*, Iron and Steel Inst. (1928) 17, 109.

The Constitution of the Iron-silicon Alloys, Particularly in Connection with the Properties of Corrosion-resisting Alloys of This Composition*

By M. G. CORSON, NEW YORK, N. Y.

(New York Meeting, February, 1928)

THE iron-silicon alloy series has always been one of the most puzzling among the binary alloys. Examining the well-known mechanical properties of the iron-rich alloys only we meet the following situation:

The ultimate strength and yield point of alloys worked and annealed under the usual conditions represent nearly a straight line function of the silicon content up to 4.5 per cent. silicon (Fig. 1). Starting at the ultimate strength of 35,000 lb. and at a yield point of 16,000 lb. for pure electrolytic iron, one reaches a maximum strength of 93,000 lb. and a maximum yield point of 74,000 lb. at 4.5 per cent. silicon. This corresponds to an increase in ultimate strength by 13,000 lb. per each per cent. of silicon added and nearly the same rate applies to the yield point. The data mentioned are taken from the investigation by T. D. Yensen,¹ and while they do not exactly corroborate the results obtained by earlier investigators, they seem to be the most correct.

Plastic properties of the alloys are controlled by a much more complicated relationship. Up to 2.5 per cent. Si, the elongation stays close to 50 per cent. (in 2 in.) and the area reduction amounts to 85 per cent., a situation that forms the usual feature of all alloys representing strictly solid solutions. The plasticity of the latter is always nearly equal to that of their base metal.

Beyond 2.5 per cent. silicon, the situation becomes much more complicated. Yensen observed an enormous drop in elongation and area reduction at about 2.65 per cent. silicon, where the first hardly reaches 10 per cent. and the second is still lower; he found, however, a considerable recovery in plasticity at about 2.8 per cent. Si and up to 4.5 per cent. Si it is represented by 20 per cent. for the elongation and 30 per cent. for area reduction.

Yensen's graphs, as shown in Fig. 1, indicate also a considerable drop in strength and yield point at the same point of 2.65 per cent. Si,

* Investigation accomplished by the author in service of the Duriron Co., Dayton, Ohio.

¹ T. D. Yensen: Magnetic and Other Properties of Iron-silicon Alloys Melted in Vacuo. Eng. Exp. Sta., Univ. Illinois. Bull. 83 (1915).

which observation, if true, would mean that a discontinuity takes place at this point for all mechanical properties. The author of this report reinvestigated alloys with 2.65 per cent. silicon but was not able to notice the minimum in strength and ductility indicated by Yensen. Therefore he feels compelled to draw the conclusion that Yensen met with some incidental condition which has been responsible for the deleterious effect upon the mechanical properties. Still, and at any rate, there can be no doubt that some change in the intimate nature of the alloys, resulting in a sharp decrease in plasticity, takes place beyond 2.5 per cent. silicon.

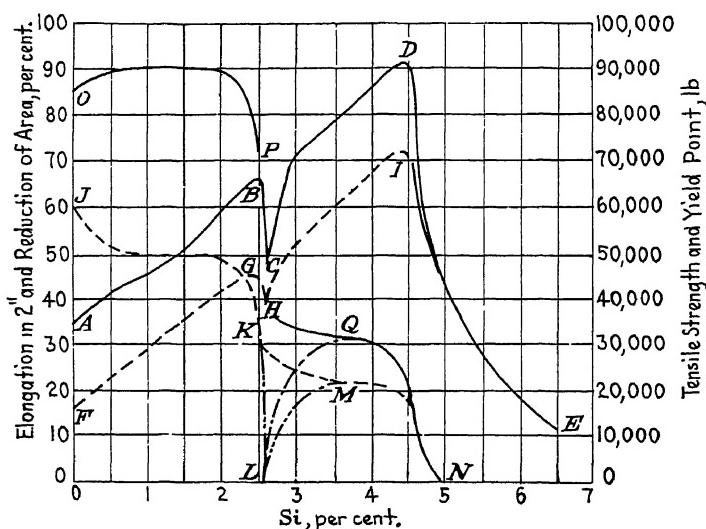


FIG. 1.—REPRODUCTION OF GRAPHS PLOTTED BY T. D. YENSEN.

After reaching 4.5 per cent. silicon, we find again a definite drop in strength and plasticity. According to Yensen, the ultimate strength of the forged and annealed alloys is as low as 43,000 at 5 per cent. silicon, the yield point coinciding here with the ultimate strength. At the same time the features of plasticity—*i. e.*, plastic elongation and area reduction—drop to zero. Finally, Yensen, as well as the older authorities, found the alloys beyond 6 per cent. silicon to be entirely unworkable either hot or cold.

These mechanical properties considered alone would not represent anything particularly astonishing. They could be interpreted as indicating that up to 2.5 per cent. silicon the alloys represent a strictly stable solid solution, while beyond this point a second much less ductile constitutional element is formed, its presence introducing a certain stiffening

of the alloy without interfering at all with the ultimate strength and the yield point up to 4.5 per cent. silicon. They might indicate also that beyond this latter point the presence of the secondary constituent becomes predominating and the alloy develops brittleness.

Nothing of this kind has been indicated, however, from the results obtained by the investigators who worked along the development of the constitutional diagram of the iron-silicon alloys. Guertler and Tammann² were the first among these investigators and they found that up to 19.8 per cent. silicon the alloys represent a solid solution while at the latter point the solid solution is identical with the compound Fe_2Si (Fig. 2).

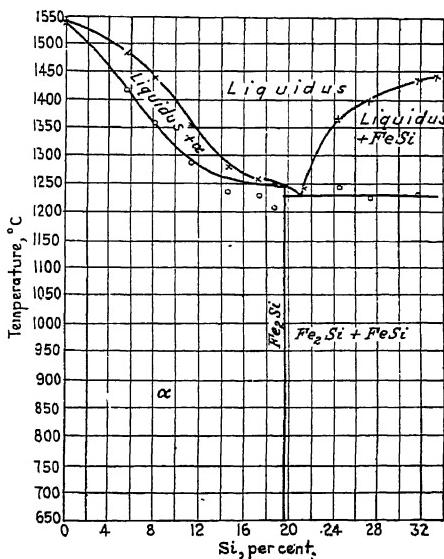


FIG. 2.—DIAGRAM OF GUERTLER AND TAMMANN.

Now all our knowledge of those well-studied alloy systems which include a wide range of solid solutions at the ductile element's end of the diagram shows that no discontinuity in the properties of such alloys can be observed until the solid-solubility range is passed. Usually, the strength, yield point, hardness and electric resistivity will increase along with the increase in the content of the added element. This increase does not have to follow a straight line relationship and may even stop after a certain level is reached, but in no case has a decrease in the same properties been observed.

² W. Guertler and G. Tammann: Über die Verbindungen des Eisens mit Silicium. *Ztsch. f. anorg. Chem.* (1905) **47**, 163.

The investigation by Guertler and Tammann was followed by those of Gontermann,³ Sanfourche,⁴ Kurnakow and Urasow,⁵ and Murakami⁶ (Figs. 3-6). Kurnakow's diagram (Fig. 3) did not differ much from that of Guertler; he found, however, none of the compound Fe_2Si . Gontermann again introduced certain alterations within the solid-solution range (Fig. 4) but did it in a most hypothetical manner, presenting no proof of

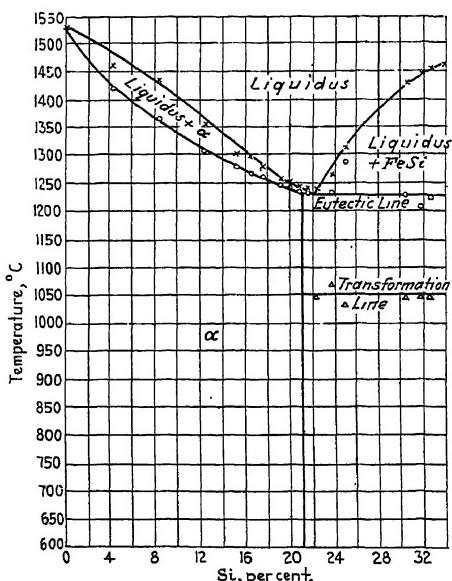


FIG. 3.—KURNAKOW'S DIAGRAM.

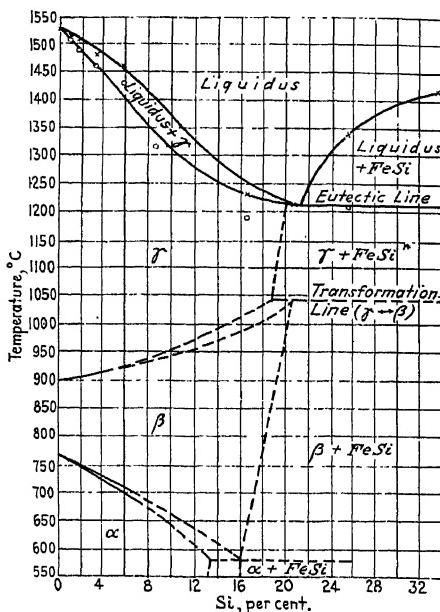


FIG. 4.—GONTERMANN'S DIAGRAM.

any kind. At any rate, he also believed that up to 20 per cent., silicon will form a solid solution in iron, at least near the melting point; *i. e.* 1235° C. The solid solutions were believed by Gontermann to pass through a series of transformations, namely: (1) from homogeneous gamma crystals to a duplex structure of gamma plus beta, (2) next to a uniform beta, (3) then to a mixture of beta plus alpha and finally (4) to pure alpha. In the latter state, according to Gontermann, there comes

³ W. Gontermann: Bemerkungen zum System Eisen-Silicium. *Ztsch. f. anorg. Chem.* (1908) **59**, 384.

⁴ M. A. Sanfourche: Contribution à l'étude des ferro-siliciums. *Rev. de Mét. (Mem.)* (1919) **16**, 217.

⁵ N. Kurnakow and G. Urasow: Togische Eigenschaften des Ferrosiliciums des Handels. *Ztsch. f. anorg. Chem.* (1922) **123**, 89.

⁶ T. Murakami: On the Equilibrium Diagram of the Iron-silicon System. *Sci. Rept. Tohoku Imp. Univ.* (1921) **10**, 79; Further Investigation of the Equilibrium Diagram of the Iron-silicon System. *Op. cit.* (1927) **16**, 475.

a solid solubility limit of about 12 per cent. silicon only. However, even the diagram so changed does not explain the intricate manner in which the mechanical properties change with the increase in the silicon content.

The more recent diagram made by Murakami (Fig. 6) gives no evidence of the transformations in the solid state, but contains a rather sharp definition of the solid-solution range. According to Murakami, all alloys below 22 per cent. silicon crystallize as solid solutions, while above this point the first constituent to crystallize is the compound FeSi, which is followed at 1190° C. by a eutectic built up of some FeSi plus the 22 per

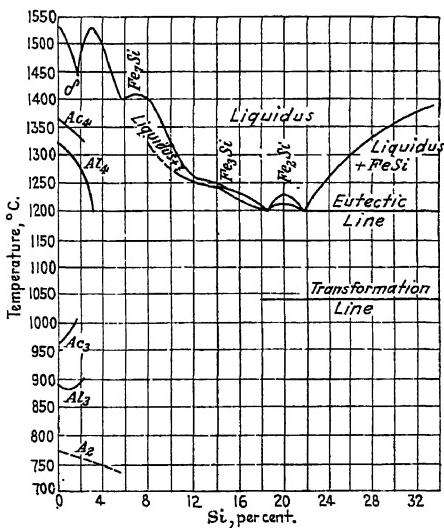


FIG. 5.—SANFOURCHE'S DIAGRAM.

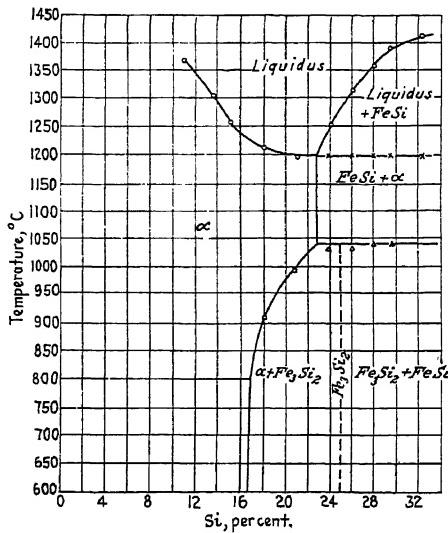


FIG. 6.—MURAKAMI'S DIAGRAM.

cent. silicon solid solution. This condition lasts until the temperature of 1040° is reached, when all alloys from 16.5 to 22 per cent. silicon begin to precipitate the compound Fe_3Si_2 , and the solid-solution range becomes more and more narrow until it reaches a temperature of about 750°, below which it contains 16.5 per cent. silicon only.

The thermic behavior of alloys above 22 per cent. silicon indicates, according to Murakami, the same reaction between the solid solution with 22 per cent. silicon and the compound FeSi, which causes them to form, at 1040°, the compound Fe_3Si_2 . For an alloy containing exactly 24.8 per cent. silicon, therefore, a strictly uniform monophase structure representing the compound Fe_3Si_2 must be obtainable. Beyond this composition some FeSi remains unaffected by the reaction and the structure remains duplex.

Leaving out of consideration alloys containing more than 16.5 per cent. silicon, we find this composition, representing, according to Murakami, the limit of solid solutions, and again the constitutional diagram fails entirely to explain either the brittleness of iron-silicon alloys beyond 4.5 per cent. silicon, or the general discontinuity in the mechanical properties of the alloys in this range.

Most recently Oberhoffer⁷ reexamined the same system, using the dilatometric method. He did not go beyond 2.41 per cent. silicon, and so found only that the presence of silicon affects in the most definite way both the A₄ point of transformation of delta iron (body-centered cubic

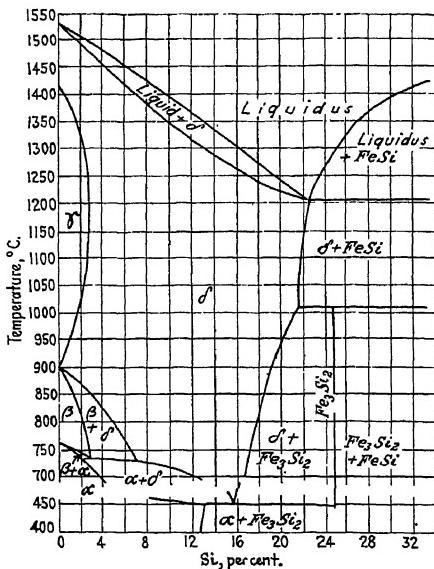


FIG. 7.—FE-SI DIAGRAM AS DEVELOPED BY W. GUERTLER.⁸

crystals stable above 1400° C.) into gamma iron (face-centered cubic crystals) and the point A₃ (910°) of the gamma to alpha transformation (the alpha being identical with the delta). The first point is lowered and the second raised until they meet somewhere between 1100° and 1250° C. The field in which gamma iron may exist as a single phase becomes in this way confined to between 0 and 2.5 per cent. silicon, according to the temperature. Beyond the latter point, according to Oberhoffer, there is nothing but delta (or alpha) iron containing in solid solution anywhere from 2.5 to 18 per cent. silicon. This last limit of silicon concentration in the solid solution is considered by Oberhoffer to remain constant through the whole temperature range 1235° to 0° C.⁹

⁷ H. Esser and P. Oberhoffer: Zur Kenntnis der binären Systeme Eisen-Silizium, Eisen-Phosphor und Eisen-Mangan. Ver. deut. Eisenhüttenleute, Werkstoffausschuss Berichte (1925) 69; *Stahl und Eisen* (1924) 44, 979.

⁸ *Stahl und Eisen* (1922) 42, 667.

CRITICISM OF THE DIAGRAMS OF PREVIOUS INVESTIGATORS

1. Tammann and Guertler's diagram:
 - a. Alloys below 5.5 per cent. silicon not included.
 - b. Micrographic and physical tests practically lacking.
2. Gontermann's diagram:
 - a. No alloys between 9 and 16 per cent. silicon studied.
 - b. Micrographic and physical tests practically lacking.
3. Kurnakow's diagram:
 - a. In spite of the fact that an alloy with 15 per cent. silicon was examined by Kurnakow micrographically at 100 dia. shows definitely a second constituent around the grain boundaries; and
 - b. In spite of the fact that an alloy with 20.6 per cent. silicon as examined by Kurnakow micrographically at 100 dia. shows an absolute lack of homogeneity; and
 - c. In spite of the fact that the alloy with 15 per cent. silicon showed a definitely low liquidus point—by 25° lower than the corresponding point upon the plotted liquidus curve—the limit of solid solubility was placed at 21 per cent. silicon.
4. Sanfourche's diagram:
 - a. This suffers from a clearly noticeable tendency to hunt for "compounds."
5. Murakami's diagram:
 - a. No alloys below 11 per cent. silicon were studied.
 - b. Micrographic proofs for the solid-solubility range are lacking.
 - c. Micrographic proofs of a change from a homogeneous solid solution forming a precipitate of a secondary constituent if the composition runs from 16.5 to 22.5 per cent. silicon are lacking.
 - d. Micrographic proofs are lacking that heating up or near to 1040° C. renders homogeneous alloys containing about 25 per cent. silicon.
6. Oberhoffer's diagram:
 - a. No alloys above 3 per cent. silicon were studied.

No constitutional diagram hitherto traced accounts for the particular effects of silicon upon the mechanical properties of iron, and none has been established in a decisive manner.

With this in mind the author started his own investigation. Possessing no facilities whatsoever to reinvestigate the curves of the incipient fusion (solidus) and the complete liquefaction (liquidus) he was obliged to limit himself in this direction to a critical examination of the curves obtained by previous investigators. His main interest has been concentrated (1) in the direction of transformations taking place in the solid

state and (2) in the concentration range of the solid solutions. The critical examination of other diagrams helped, however, to form an opinion about the general conclusions of the previous investigators.

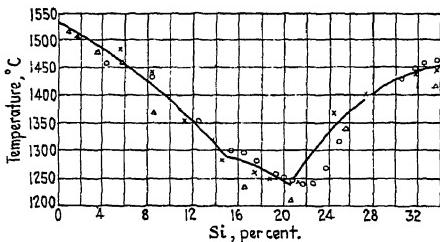


FIG. 8.—LIQUIDUS LINE OBTAINED BY AVERAGING THE DATA OF TAMMANN, KURNAKOW AND GONTERMANN.

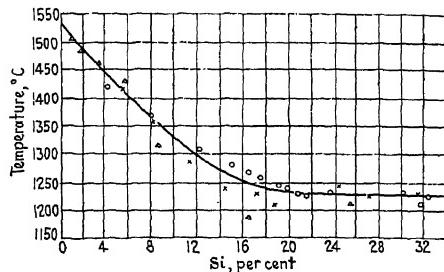


FIG. 9.—SOLIDUS LINE OBTAINED BY AVERAGING THE DATA OF TAMMANN, KURNAKOW AND GONTERMANN.

For this purpose Figs. 8 and 9 were drawn representing the points of the liquidus and solidus respectively as found by Tamman, Kurnakow and Gontermann. Gontermann's liquidus points are usually lower than those of Tamman and Kurnakow, and some of the first had to be entirely

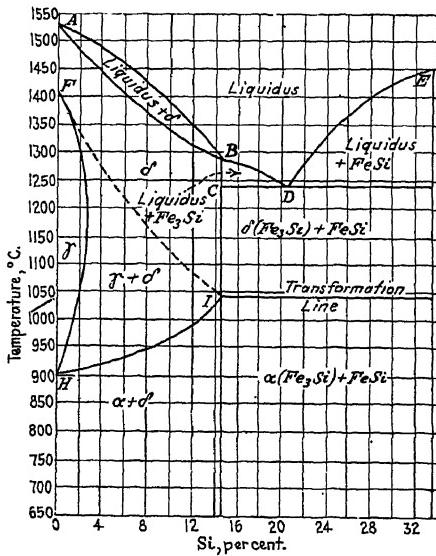


FIG. 10.—DIAGRAM BASED ON COMBINATION OF LIQUIDUS AND SOLIDUS LINES TRACED THROUGH HARMONIOUS POINTS OF FIGS. 8 AND 9.

discarded. Using the points which do not show any unexplainable discrepancy, a new variant of the liquidus and solidus lines was traced. Combination of these two resulted in the diagram shown in Fig. 10. In this way the author became convinced of the following: (1) there is a

definite break in the liquidus curve about 14.5 per cent. silicon; (2) the solidus line meets the liquidus at $1285^\circ \pm 5^\circ$; (3) all points obtained by the previous investigators and distributed at random around the line of 1230° C. correspond to the crystallization of the eutectic, while the eutectic itself must be located somewhere around 20 per cent. silicon.

Should the conclusions so obtained (from the examination of old diagrams) be true, the concentration limit of the solid solution may not go beyond 14.5 per cent. silicon even near the melting point, while its ranges at lower temperature remain to be found.

But again the allocation of this point of 14.5 per cent. silicon as the concentration limit of the solid solution at one temperature or another does not yet produce an explanation for the brittleness and the general deviation of the iron-silicon alloys from the law of continuity. Consequently one of two lines of reasoning must be followed: Either such alloys become hopelessly contaminated, when made under any given condition (including vacuum melting), or something is wrong with our ideas concerning the constitutional features of the solid state of these alloys. The fact that T. D. Yensen obtained brittle alloys above 5 per cent. silicon even when working in a vacuum does not yet eliminate the idea of contamination. In his case the alloys were allowed to freeze in the furnace and therefore might have developed very large crystals with a comparatively small total intercrystalline surface. This circumstance in its turn might permit a comparatively small contamination to spread itself as a more or less thick film around all crystals. The only two contaminations logically possible are oxides (or silicates) or nitrides, since in alloys made out of reach of carbon only elements that exist in the air can be introduced.¹⁰

With this idea in mind the author made a number of alloys of varying silicon content and has kept them for variable intervals of time in contact with air at temperatures ranging from 1270° to 1500° C. In some experiments nitrogen and air were blown through some of the melts. All alloys were cast in the shape of bars $\frac{1}{2}$ in. square and 12 in. long, using both chills (graphite) and sand molds. The bars were afterwards tested in the cantilever test. For this purpose they were fixed horizontally in the usual tensile-test machine, using special grips, and the load was applied at their free end at a 1 in. distance from the fixed point.¹¹

Having obtained one fracture, the bar was always pushed out far enough to load it again in the same way and to obtain a second fracture, etc. Usually from six to seven fractures were obtained on each bar and the breaking loads averaged. Low figures corresponding to defects in the fracture were eliminated. The results proved definitely that there is not even the slightest connection between the breaking strength and

¹⁰ Provided the melting is done in sand or magnesia crucibles.

¹¹ See Appendix 3.

the contamination with either oxygen or nitrogen; also that the melts through which nitrogen was blown had a definitely higher strength. The increase in strength obtained in this case was not, however, sufficiently high to explain the usual brittleness of iron-silicon alloys by the presence of films of oxide which might have been removed by the bubbling nitrogen, since in no case was the brittleness eliminated to any truly remarkable degree.

These tests lead to the conclusion that the brittleness cannot be explained by contamination and must be accounted for by the particular constitutional features of the alloys.

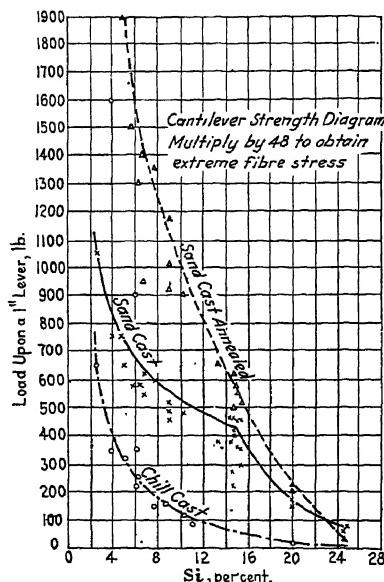


FIG. 11.—DATA ON CANTILEVER TEST PLOTTED IN THEIR RELATION TO SILICON CONTENT OF CHILL-CAST BARS.

All chill-cast bars were weak, much more so than those obtained in sand molds, although usually chill-cast industrial alloys are much stronger because their grain is more refined. All chill-cast bars containing above 8 per cent. silicon cracked partly in the mold and it was difficult to obtain any definite figures for their breaking strength in the cantilever test. The data on these tests have been plotted in their relation to the silicon content in Fig. 11.

The next step was to find by means of some physical tests, the actual constitutional features of the iron-silicon series. For this purpose we used the electric resistivity, Rockwell hardness and finally micrographic and macrographic tests.

ELECTRIC-RESISTIVITY TESTS

The electric resistivity of alloys forming solid-solution ranges may be represented by three types of theoretical curves. In one case the electric resistivity of one pure metal increases continuously upon the addition of a second component and reaches a point where the continuous run of the curve ceases and a break ensues. This is the point where the solid solution reaches its limit of concentration. Beyond this point there is usually a different type of curve, quite flat in shape, which corresponds to a mixture of the first solid solution with a second constituent. In the second case the resistivity reaches a certain level and stays there through a range of compositions. This case cannot be definitely explained and the "constant level" part of the curve may be due either to the cessation of

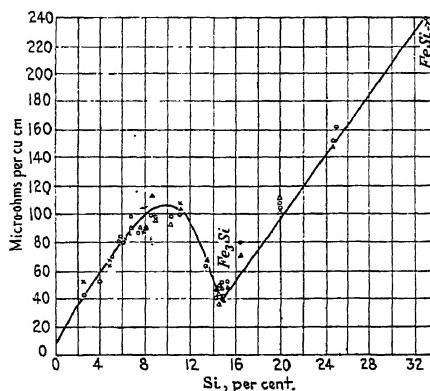


FIG. 12.—ELECTRIC RESISTIVITY OF SAND-CAST BARS.

Values obtained in sand-cast state are indicated by x; chill-cast, o; annealed, Δ.

that influence of the second element which causes binding of the free electrons or to the presence of a secondary constituent with a conductivity identical with that of the first solid solution.

Finally, in cases where the resistivity curve shows a maximum and then drops in a continuous way with no break recorded anywhere, we find a continuous solid solubility between the first element and either a second element or a definite chemical compound. This type of curve is most familiar when two metals form a continuous solid solution; it happens presumably in the binary series copper-nickel, copper-manganese, gold-silver, gold-platinum, etc.¹²

Our tests of electric resistivity were made on chill-cast and sand-cast bars $\frac{1}{2}$ in. square and on round bars $\frac{3}{4}$ in. dia. (sand cast). The chill-cast and sand-cast bars did not differ much in their electric resistivity

¹² The author does not believe at all in the actual existence of continuous solid solutions.

until the concentration of 8 per cent. silicon had been reached. Beyond this point, however, the chill-cast specimens showed a rather erratic behavior. The sand-cast bars gave much more definite and constant results and the ensuing diagram (Fig. 12) is represented by a curve with a maximum at about 10 per cent. silicon and a minimum around 14.5 per cent. silicon. Beyond this range the resistivity increases quickly, the resistivity graph running in an almost straight line from 37 microhms at 14.3 per cent. to approximatively 240 microhms for the FeSi compound. A minimum so sharp may represent nothing else but a definite chemical substance, and it is easy to compute its formula as being Fe_3Si with a silicon content of 14.3 per cent. This figure coincides rather definitely with the discontinuity point traced in the liquidus line, as mentioned before.

HARDNESS TESTS

The shape of the hardness graph is also a very definite indication of the nature of an alloy. For a rough mixture of two constituents it is usually a more or less straight line, while in a solid solution it is always a curve, concave to the line of composition. When two soft (ductile) metals form a continuous solid solution from one end to another, this curve has a maximum. In a solid solution between a soft metal and a hard chemical compound, the maximum corresponds to the latter, and when the limit of solid solution does not correspond to a definite chemical substance, as with brasses and bronzes, the maximum hardness is reached somewhat in advance of the concentration limit of the solid solution (as derived from microscopical examination data) and remains constant until the second constituent appears.

The usual method of hardness testing with the Brinell apparatus cannot be applied to iron-silicon alloys, because the imprints under a load of 500 or 1000 kg. are too fine, while the cast samples of alloys beyond 6 per cent. Si break invariably when the load upon the 10-mm. ball goes beyond 1000 kg. This made it necessary for the author to measure the hardness with the Rockwell apparatus only, using a load of 150 kg. and the diamond-point penetrator. The Rockwell data so obtained are plotted in Fig. 13. They show that the hardness curve rises continuously up to 14.5 per cent. silicon, where it reaches 52 Rockwell. Beyond this point it is followed by an almost straight line bent slightly downward. Again it corresponds closely to the situation that could be foreseen for alloys formed of solid solutions between iron and the Fe_3Si compound, and mixtures of the latter with a secondary constituent.

The facts mentioned make it practically certain that all alloys up to 14.5 per cent. silicon represent a continuous change from iron in which

silicon is dissolved to the compound Fe_3Si , which absorbs a certain amount of metallic iron. This would explain also the brittleness of the higher silicon alloys, since one cannot expect the Fe_3Si compound to possess much ductility even though a certain excess of iron should be absorbed in it.

Still, there remain a few points that cannot be fully explained by this assumption. The first is, that since the maximum of electric resistivity corresponds approximately to 11 per cent. silicon, one might expect alloys below 11 per cent. to represent a simple case of a solid solution of

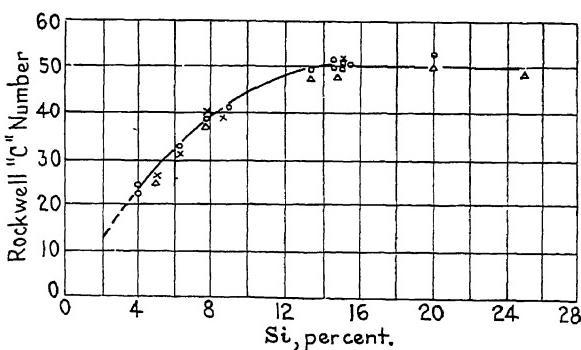


FIG. 13.—ROCKWELL HARDNESS CURVE FOR IRON-SILICON ALLOYS.
Values obtained in sand-cast state are indicated by x; chill-cast, o; annealed, Δ.

silicon in iron and consequently to be sufficiently ductile. This is not, however, the case. The Fe-Si alloys lose their plasticity in the cold state with as small an amount as 5 per cent. silicon. Consequently, additional facts must be sought to explain the situation.

MICROSCOPIC STUDY AND PHOTOMICROGRAPHS

These additional facts were obtained through the medium of the microscopic study of the alloys. In this direction the author is indebted to Mr. Vilella, of the Union Carbide and Carbon Research Laboratories, who discovered a method of etching Fe-Si alloys that revealed facts previously unknown about their structure. The etching reagent was made up of 2 parts of glycerol, 2 parts hydrofluoric acid (30 per cent.) and 1 part nitric acid. This is the reagent developed by Vilella for the etching of aluminum alloys.

An alloy with 2.5 per cent. silicon shows nothing particular except grains of a solid solution, some bright, some gray and some quite dark. No definite conclusion can be drawn from this photomicrograph. The experience of the author, however, has been that the grains in a real solid solution are rather bright; therefore the author suggests that even

alloys so low in silicon do not represent a perfect solid solution. Fig. 14 shows an alloy with 4 per cent. silicon in the forged and annealed state. The general aspect remains the same but some additional mottling of



FIG. 14.—HEAT 38; 4.0 PER CENT. Si, FORGED, ANNEALED. $\times 100$.

the surface accentuates the suggestion that some subtle process has taken place in these alloys.

6 Per Cent. Silicon Alloy

Figs. 15 to 20 represent the structures of a 6 per cent. Si alloy in various states. Fig. 15 corresponds to the sand-cast state. In addition to the grains of a solid solution, there are present some fine but rather definite marks looking more or less like barley shells; these markings as well as the grains are more definite and larger in the sand-cast than in the chill-cast state. Figs. 16 and 17 represent the same alloy, chill cast and sand cast, but at a higher magnification. The grain boundaries here are not really plain lines, as usual in solid-solution alloys, but are built up of some secondary constituent. The "barley shell" markings

FIG. 15.—HEAT 23; 5.9 PER CENT. Si, SAND CAST. $\times 100$.FIG. 16.—HEAT 24; 6.1 PER CENT. Si, CHILL CAST. $\times 500$.FIG. 17.—HEAT 23; 5.9 PER CENT. Si, SAND CAST. $\times 500$.

do not possess definite boundaries; *i. e.*, do not represent a definite secondary constituent. In some spots the alloy shows a few fine whitish crystals within a mottled groundmass.

Keeping the alloys at high temperatures with 6 per cent. silicon for varying periods of time, followed by either quenching or slow cooling produces a variety of structures depending upon the method of casting,

18



19



FIG. 18.—HEAT 24; 6.1 PER CENT. SI, CHILL CAST 6 HR. AT 950° C., WATER-QUENCHED.
X 100.

FIG. 19.—HEAT 23; 5.9 PER CENT. SI, SAND CAST 6 HR. AT 950° C., AIR-COOLED.
X 100.

time and temperature of heating and the speed of quenching or cooling. So Fig. 18 represents an alloy where the markings became definitely increased, and where the grains contain a fine precipitate. In Fig. 19 the precipitate is more definite, but the markings have practically disappeared. The grain boundary persists in carrying some secondary substance just as mentioned before for the raw cast state. Samples

obtained by quenching some of the chill-cast alloy from a higher temperature showed a partial preservation of the precipitate, while the structure became, in general, "troostitic." Some markings of the barley shell type remain and in spots they form brushes radiating in every direction. These brushes usually start from a small crystal-like particle, as can be seen in Fig. 20. In a sample chill cast and annealed for a long time at 950° C., with a particularly long cooling period between 900° and 800° C., the markings disappeared completely and the alloy looked more or less



FIG. 20.—HEAT 2; 6.26 PER CENT. SI, CHILL CAST 2 HR. AT 1100° C., WATER-QUENCHED.
X 500.

like the one with 4 per cent. silicon, shown in Fig. 14. The grain boundaries, however, are more nearly straight lines, as would befit a substance that has a considerably increased hardness and does not deform too easily.

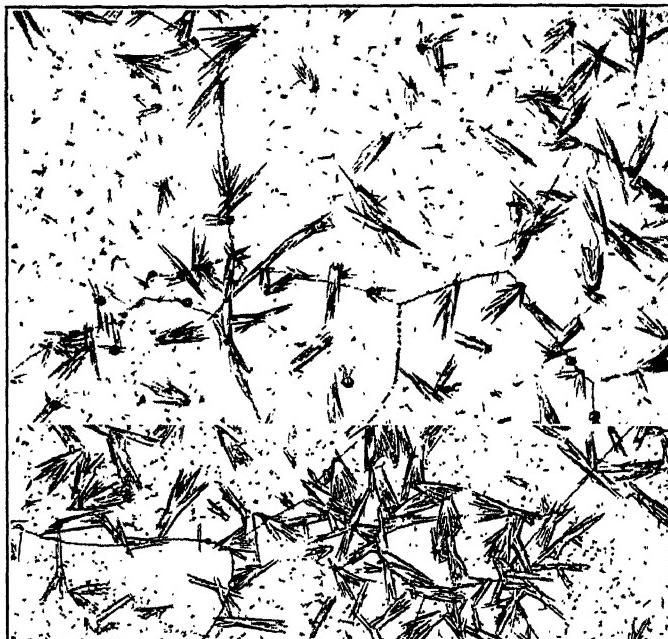
8 Per Cent. Silicon Alloy

Figs. 21 to 28 represent the structures of an alloy with 8 per cent. silicon. The sand-cast sample shown in Fig. 21 exhibits fewer markings than the chill-cast sample in Fig. 22. Fig. 23 corresponds to Fig. 22, but was obtained at a magnification of 500 under conical illumination. It is evident that the brushlike markings cannot correspond to a second

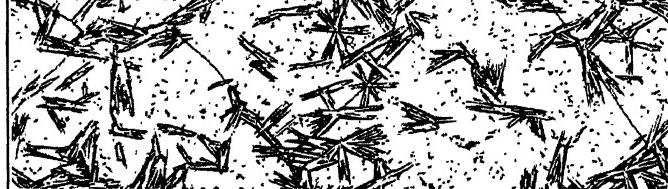
constituent, since their boundaries are not sharp enough, but represent depressions and elevations in the groundmass.

Quenching under various conditions may increase the general "brushiness" enormously, as shown in Fig. 24, or produce large brushes breaking in spots through the grains of the groundmass, which contain a well defined precipitate (Fig. 25). Since all samples have been tested

21



22

FIG. 21.—HEAT 21; 7.7 PER CENT. Si, SAND CAST. $\times 100$.FIG. 22.—HEAT 22; 7.9 PER CENT. Si, CHILL CAST. $\times 100$.

as cast and consequently their crystallization proceeded in an uncontrollable way, it has been found nearly impossible to duplicate the same type of structure by the same heat treatment. However, a very long treatment at certain temperatures, for instance 1000°, followed by slow cooling decreased considerably the frequency of the markings and also eliminated the precipitate within the grains. Finally, in an alloy forged

at about 1000° C. and air-cooled (Fig. 26), there are no brushes at all. The whole area of each grain is covered by an unmistakable precipitate very similar in appearance to coalesced cementite in carbon steels.



FIG. 23.—HEAT 22; 7.9 PER CENT. Si, CHILL CAST, CONICAL ILLUMINATION. $\times 500$.

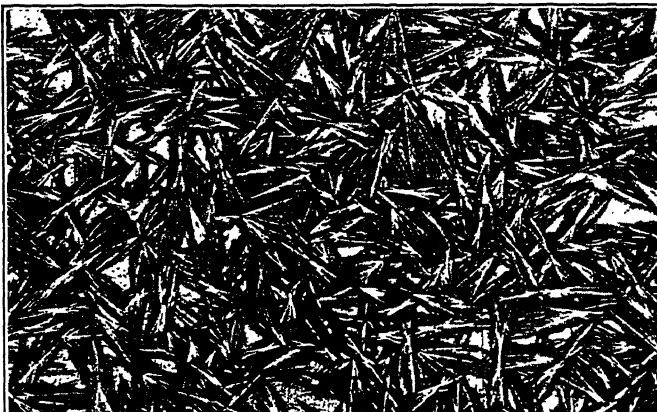
Alloys with More than 10 Per Cent. Silicon

A chill-cast alloy with 10.3 per cent. silicon was nearly as full of brushes as the alloy shown in Fig. 24. A further addition of silicon tends, however, to diminish the brushes and in an alloy with 11.1 per cent. silicon, they become rather scarce and are always confined to cracks running through the grains, as shown in Figs. 27-29. In most cases, the alloys show also an unmistakable precipitate within the grains.

Going further with the addition of silicon, we arrive at about 12.5 per cent. of the latter, to alloys which are entirely free from the brush or barley-shell markings but which, under certain conditions, possess a sharp striation within the individual grains. This is shown in Fig. 30. Long heating at 950° eliminated the striation almost completely. Incidentally, there occurs a chemical segregation in the cast bar; in such cases the outside layers will become iron rich and show chains of barley-shell markings (Fig. 31) while the more silicon-rich core will exhibit a precipitate (Fig. 32).

Next we come to an alloy containing about 14.8 per cent. silicon (Figs. 33 to 38). Under a low magnification, the structure may be mistaken for

24



25



25a



FIG. 24.—HEAT 22; 7.9 PER CENT. Si, CHILL CAST 6 HR. AT 1050° C., WATER-QUENCHED. $\times 100$.

FIG. 25.—HEAT 21; 7.7 PER CENT. Si, SAND CAST 8 HR. AT 1000° C., WATER-QUENCHED. $\times 100$.

FIG. 25a.—HEAT 22; 7.9 PER CENT. Si, CHILL CAST 2 HR. AT 925° C., WATER-QUENCHED. $\times 100$.

FIG. 26.—HEAT 22; 7.9 PER CENT. SI, CHILL CAST, HOT-FORGED, AIR-COOLED. $\times 100$.FIG. 27.—HEAT 20; 11.1 PER CENT. SI, SAND CAST. $\times 100$.FIG. 28.—HEAT 20; 11.1 PER CENT. SI, SAND CAST. $\times 500$.

a strict case of a solid solution. That is exactly the mistake made by Kurnakow¹³ when examining one of his 15 per cent. Si samples. At higher magnifications, however, the boundaries are rather thick and built up of a secondary constituent. No definitely visible secondary constituent appears in cast alloys containing above 6 per cent. and below 14 per

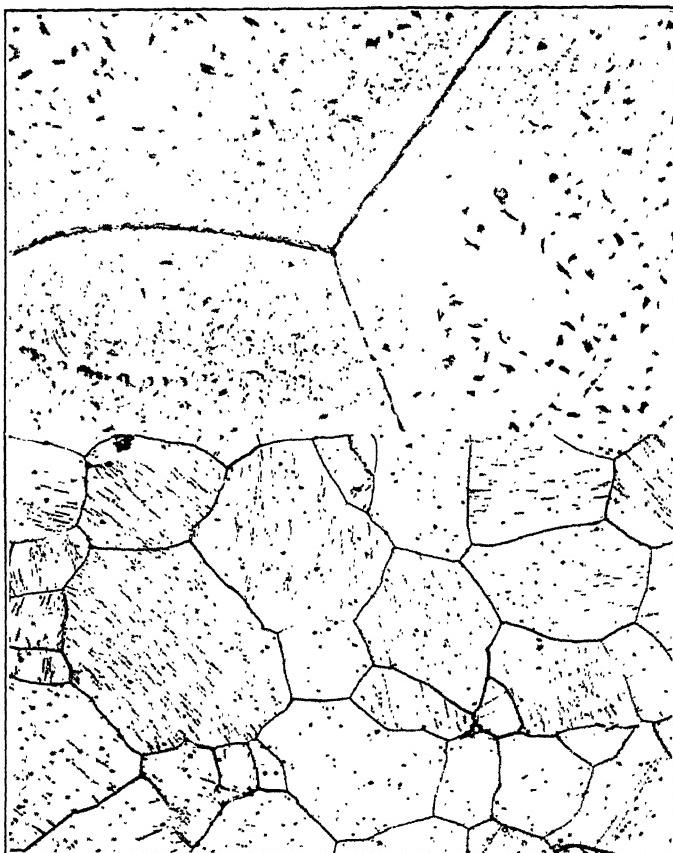


FIG. 29.—HEAT 21; 11.1 PER CENT. SI, CHILL CAST. $\times 500$.
FIG. 30.—HEAT 75; 13.2 PER CENT. SI, SAND CAST. $\times 100$.

cent. silicon, and if any is present, it can be eliminated in a 14.4 per cent. Si alloy by a prolonged heat treatment at 1000° C. No heat treatment, however, will eliminate it from alloys containing above 14.3 per cent. silicon. The size of the particles of the boundary constituent may decrease, since there is no doubt that in the cast state a real equilibrium is not fully reached. They will not, however, disappear completely even

¹³ *Loc. cit.*

after a 24-hr. treatment at 1000°. This again proves the following contentions:

Conclusions from Microscopic Study

1. The solid-solution limit in the iron-silicon alloys corresponds definitely to 14.3 per cent. silicon.
2. This limit remains constant at any temperature up to 1050° C. at least, and no additional silicon can be dissolved under any conditions. If the latter were possible, according to the diagram of Murakami (Fig. 6), a slow cooling of an alloy specimen containing 16 or 17 per cent. silicon ought to definitely produce a precipitate of a secondary constituent within the original grains. This precipitate would be rather dense, since an alloy with 16 per cent. silicon must be built up in the equilibrium state of 91 per cent. Fe_3Si and 9 per cent. FeSi . Nothing of the kind has been observed for any of the author's alloys containing between 14.5 and 18 per cent. Si; they exhibited structures unchangeable by any heat treatment. The secondary constituent formed during solidification always remained practically intact and no precipitation took place on slow cooling from temperatures above 1100° C.

The Duplex Structure Range

We arrive now at alloys located beyond the 14.3 per cent. silicon range, and we begin by considering one with 20 per cent. silicon, as shown in Figs. 39 to 40. These two photomicrographs were obtained from a chill-cast sample and indicate a very fine eutectic structure with practically no constituent predominating. A sample heated at 1100° for 2 days and quenched in water did not change its structure at all; the latter remained just as fine and as eutectic in structure. A prolonged anneal at 1100° followed by slow cooling roughened the structure considerably. A comparison of the structure shown in Fig. 40 (at 500 dia.) with one obtained for the annealed sample at 100 dia. does not indicate any substantial change in the proportion of the bright (Fe_3Si) and the grayish constituent (FeSi). Consequently we are justified in concluding that the alloy with 20 per cent. silicon forms a eutectic that may be more or less fine or rough, according to the conditions of cooling.

The features mentioned seem to entirely eliminate the possibility of the existence of the Fe_2Si compound, at least as far as temperatures below 1100° are concerned. It is not, however, entirely impossible that a 20 per cent. Si alloy crystallizes as a compound which immediately dissociates. It is desirable to note here the structural analogy between a eutectoidally transformed 23 per cent. tin bronze and a cast 20 per cent. iron-silicon alloy.

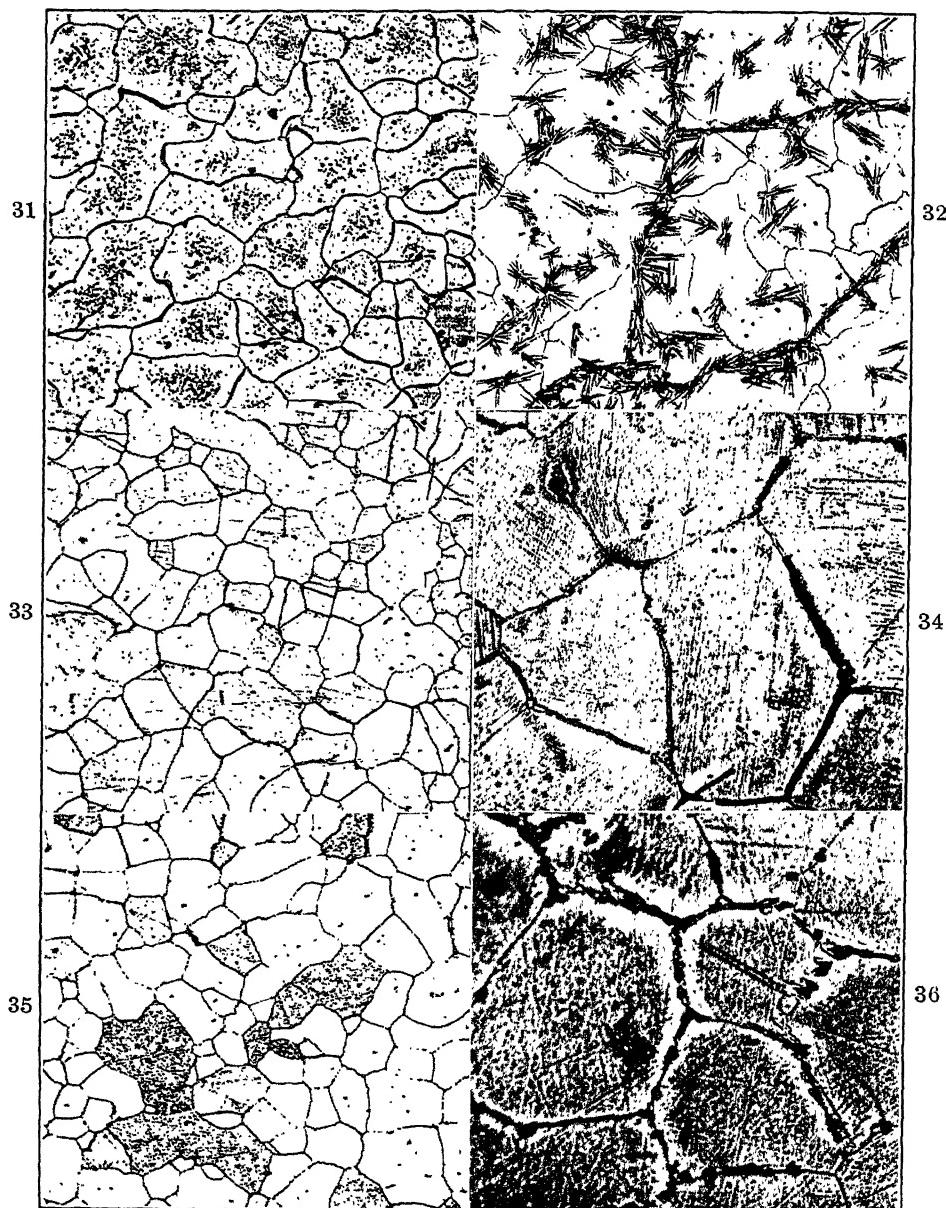


FIG. 31.—HEAT 9; 12.7 PER CENT. Si, CHILL-CAST CORE OF BAR. $\times 100$.

FIG. 32.—HEAT 9; 12.7 PER CENT. Si, CHILL-CAST EDGE OF BAR. $\times 100$.

FIG. 33.—HEAT 28; 14.7 PER CENT. Si, SAND CAST. $\times 100$.

FIG. 34.—HEAT 28; 14.7 PER CENT. Si, SAND CAST. $\times 500$.

FIG. 35.—HEAT 28; 14.7 PER CENT. Si, SAND CAST 24 HR. AT 1000° C., WATER-QUENCHED. $\times 100$.

FIG. 36.—HEAT 28; 14.7 PER CENT. Si, SAND CAST 24 HR. AT 1000° C., WATER-QUENCHED. $\times 500$.

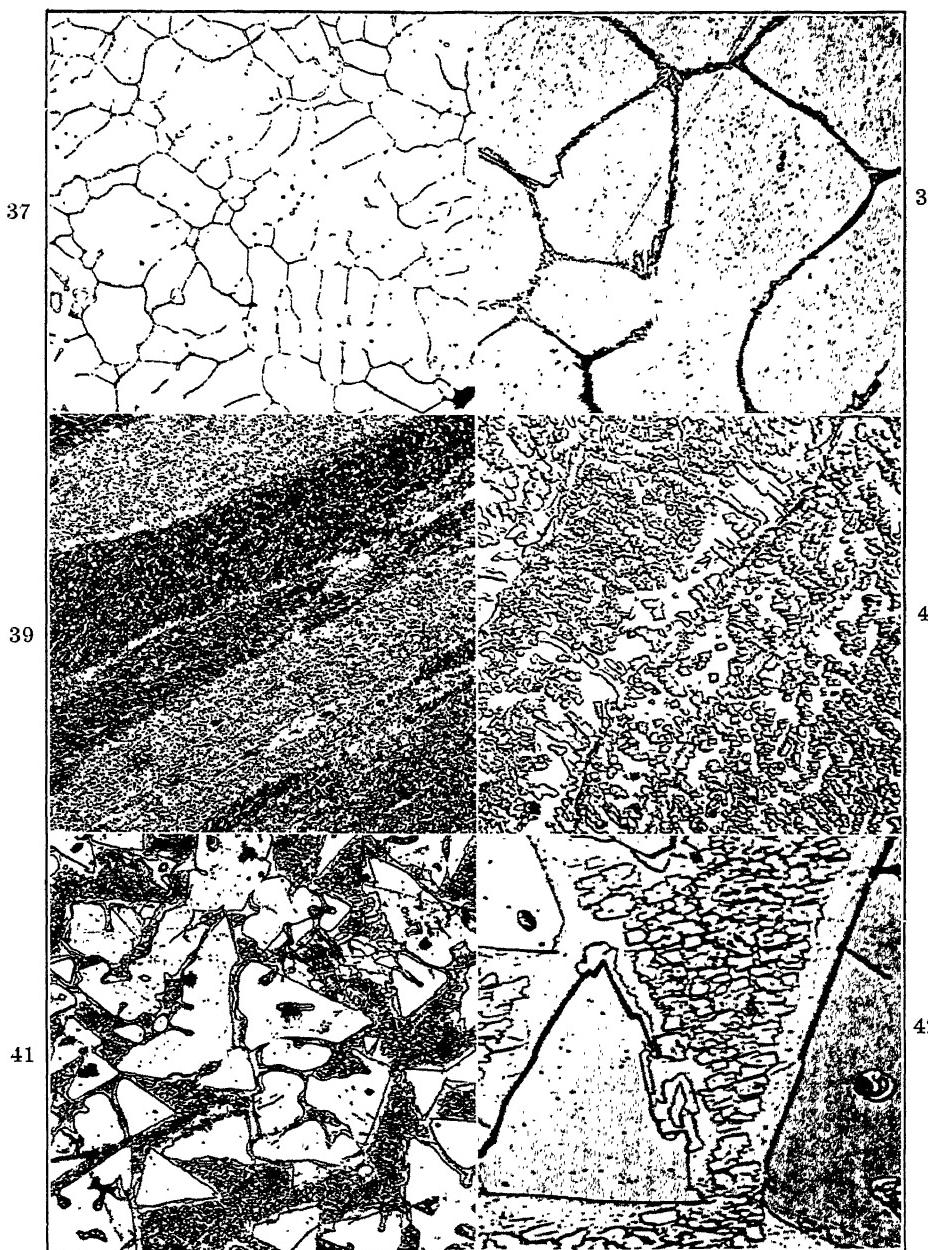


FIG. 37.—HEAT 32; 14.9 PER CENT. Si, CHILL CAST. $\times 100$.
FIG. 38.—HEAT 32; 14.9 PER CENT. Si, CHILL CAST. $\times 500$.
FIG. 39.—HEAT 7; 19.8 PER CENT. Si, CHILL CAST. $\times 100$.
FIG. 40.—HEAT 7; 19.8 PER CENT. Si, CHILL CAST. $\times 500$.
FIG. 41.—HEAT 79; 24.7 PER CENT. Si, SAND CAST. $\times 100$.
FIG. 41.—HEAT 79; 24.7 PER CENT. Si, SAND CAST. $\times 500$.

Going further, we will examine an alloy with 25 per cent. silicon. In the sand-cast state, it shows primary crystals (FeSi) embedded in a eutectic mass (Figs. 41 and 42). The author heated samples of this alloy for 16 hr. at 1050° C. and cooled them either by direct quenching in water or rather slowly with protracted stops at 1000°, 950° C., the stops being followed by quenching. The only change noticed was the roughening of the eutectic. The proportion of the primary crystals and of the eutectic mass remained nearly constant and the author never observed a change that might indicate the formation of a compound of the formula Fe_3Si_2 , as insisted upon by Murakami. Consequently we reach the conclusion that a 25 per cent. silicon alloy does not represent a compound under any possible conditions; a conclusion that is corroborated also by the run of the electric-resistivity graph, which shows no breaks at this concentration.

On the basis of these facts, the conclusion is reached that the nature of the alloys containing more than 14.3 per cent. silicon is rather simple. A compound of the formula Fe_3Si crystallizes primarily from all melts containing less than 20 per cent. silicon. At the point of 20 per cent. (plus or minus 0.50) silicon, a eutectic crystallizes in a most definite shape. Beyond this point the primary crystals represent the compound FeSi.

Recent examination of the 20 and 25 per cent. silicon alloys in the sand-cast state by the dilatometric method (using Rockwell dilatometer and 3-in. test pieces) has shown that both suffer some kind of transformation at 1025 to 1035° C. The amplitude of the transformation is considerably larger for the 20 per cent. silicon alloy and it becomes more and more evident that the actual transformation at this point must represent a eutectoidal dissociation of a "beta" phase.

The Solid-solution Range

The range below 14.3 per cent. silicon is, however, quite intricate. Upon the basis of our investigation of the electric conductivity and hardness, we might be inclined to represent it as displaying a continuous change from a solid solution of silicon in iron into a solid solution or (a better term) an absorption product of iron by the Fe_3Si compound. The graphs of hardness and of the electric resistivity do not give even an inkling as to the changes taking place in the solidified alloys. The existence of such changes, however, was most definitely recorded by the author from the microscopic examination, as narrated above. The brush-like markings, which may be noticed only incidentally in alloys containing about 4 per cent. silicon, increase continuously up to 10.5 per cent. silicon and rapidly decrease beyond this point; above 12.5 per cent., these markings were noticed only occasionally. Quenching from a high temperature (1000°–1100° C.) accentuates these markings, while quenching from temperatures slightly above 900° produces fewer markings plus a definite precipitate. Finally long heating at about 900° followed by a very slow

cooling tends to eliminate either the brushes alone or both the brushes and the precipitation. Alloys above 12.5 per cent. show only a parallel striation of a brownish shade within their grains.

These micrographic features can be explained tentatively in the following way. There is no doubt that the curve limiting the field of pure gamma in the Oberhoffer variation of the iron-silicon diagram can not stay single. Granted that the phase rule is correct, it eliminates entirely the possibility of an abrupt change of delta into gamma and gamma into alpha taking place for every composition at a single temperature point. Changes of this nature must take place in a continuous way and consequently there must be always a range where the alloy represents a mixture of gamma plus delta at higher temperature or of gamma plus alpha at lower temperatures, which is the same thing crystallographically but is not so from the viewpoint of the history of a given alloy. The latter includes two transformations in every alloy, which proceed in the following manner.

The homogeneous grain of the delta solid solution throws out in a continuous manner grainlets of gamma iron low in silicon, while the mother grain itself becomes increasingly rich in silicon. Next a reversed process takes place and the gamma becomes reabsorbed by the delta, the final product being the alpha solid solution.

This would have been the history of a very slowly cooled and fine-grained alloy. The cast state must be considered as being quite remote from the state of equilibrium. Consequently both the formation of a microscopically resolvable duplex structure and the reabsorption of gamma must be considerably delayed. The grainlets of gamma cannot, however, remain in this shape below the equivalent of the A_3 point and the grains of the cold alloy must consequently represent in its cast state a combination of a groundmass of a high-silicon delta with fine grainlets of a low-silicon alpha embedded in it. And, in a direct relation to the suddenness of the cooling, these two transformations lend the alloys their peculiar brushy structure. The more sudden the cooling, the finer the distribution of the gamma in the delta and the greater the number of brushes in the alloy, which takes on a decidedly martensitic appearance. The less sudden the cooling, the fewer the brushes and the greater the opportunity for the grainlets of gamma to coalesce before transforming into alpha. If the slowness of cooling is not sufficient to have these alpha grainlets reabsorbed by the groundmass of each grain, we obtain structures containing precipitates. A slow cooling eliminates the precipitate and the brushes to a considerable degree and a more or less normal structure of a solid solution results.

The fact that the brushes come into appearance at approximately 4 per cent. silicon causes us to conclude that the low-silicon boundary of pure gamma ought to run somewhere below 4 per cent. It is quite rea-

sonable, however, to expect that with a small content of silicon the quantitative side of the transformation of delta into a duplex gamma plus delta structure has a small magnitude and consequently the martensite-like brushes do not form; the same is true of the low-carbon steels, which do not easily turn martensitic.

At the other end of the range we find the brushes traceable in all alloys below 12.5 per cent. Si, which indicates that the duplex range ought to stretch somewhat beyond this point; it is quite possible that the brownish striation in alloys of 13.0 per cent. silicon can be accounted for by the smallness of the magnitude of the delta to gamma plus delta transformation in alloys so high in silicon.

Consequently the author believes it possible to draw in a tentative manner two lines *FI* and *HI* representing the incipient transformation of delta to gamma plus delta and the completed transformation of the gamma plus delta into alpha, as shown in Fig. 10. It is the author's belief that the crossing point of these two curves is located upon the vertical of the composition corresponding to the compound Fe_3Si .

Of these two lines, the lower one is drawn more definitely, since all alloys become homogeneous (free from brushes and precipitates) if kept sufficiently long at or near the temperature representing the A_3 point for the particular composition; all retain the brushes or precipitates when quenched from much above this point. The upper curve (dotted) is much less definite, because the author had no chance to resort to heat treatments at temperatures above 1100° C. , and the A_4 point can not possibly drop so low.

It is desirable at this point to discuss the meaning of the 1040° isotherm as observed by Murakami and explained by him as being the temperature at which the (Fe-Si) solid solution combines with the FeSi compound, forming the compound Fe_3Si_2 .

The present author emphatically denies the formation and existence of this compound and suggests that the 1040° isotherm, practically disappearing at the FeSi vertical, represents the A_3 point for the Fe_3Si compound. Hypothetically, it is not at all impossible that above 1040° the 14.3 per cent. silicon alloy represents only the limit of solid solubility, while at this temperature it suffers a rearrangement of the lattice and becomes a definite compound.

The transient range of duplex structures will explain nicely the brittleness of alloys containing more than 5 per cent. silicon. All such alloys in the cast state should possess grains, the groundmass of which contains much more silicon than corresponds to the average composition of the alloy, and consequently approaches more closely the compound Fe_3Si , which, as usual for compounds, can not be any too ductile. The more silicon an alloy contains, the nearer the composition of the groundmass

of each grain (in the cast state) is to the Fe_3Si compound, and the more accentuated its brittleness.

Chill-cast samples where this situation is only too accentuated are therefore more brittle than the sand-cast ones, and the raw sand-cast specimens are more brittle than the annealed.

Samples quenched from above 900° to 1000° are, for the same reason, still more fragile.

The suggested shape of the transformation range explains further why alloys of intermediate compositions are less resistant to corrosion than even pure iron. The grains of such alloys are formed of a high-silicon groundmass and low-silicon grainlets—sometimes of microscopically visible size, sometimes distributed in the form of brushlike masses. At such spots the potential difference between the high-silicon and the low-silicon constituents may become excessive, and sufficient to start an accelerated corrosion.

Dilatometric investigation of alloys with 5, 9, 13 and 14.5 per cent. silicon seem to yield the following data: All test pieces exhibit a range of temperature starting somewhere between 1015° and 1090° C., in which there is no dilatation on heating. The test pieces behaved in a somewhat non-reversible way, not showing any abrupt stop in contraction either at the mentioned or lower temperatures. Fig. 64 is a variation of the diagram shown in Fig. 10, which the author believes more probable in the light of his recent work.

X-RAY ANALYSIS

The foregoing conclusions were obtained with the aid of sclerometric, micrographic and electric-resistivity tests. It remained to see whether a more intimate study of the crystalline structure with the aid of X-rays would not produce another set of either corroborative or negative data.

Let us see what essential features could be expected upon the X-ray films on the basis of the previous conclusions:

1. The crystalline lattice must retain the type of the body-centered alpha iron up to the 14.3 per cent. Si concentration, the latter corresponding to the compound Fe_3Si .
2. The parameters of this lattice must undergo a continuous change.
3. New lines must appear immediately beyond 14.3 per cent. Si and increase in number and sharpness until the pure FeSi composition (33.4 per cent. Si) is reached.
4. Since our conclusions answer in the negative the question as to the formation of the Fe_3Si_2 compound at 1040° (Murakami) no change must be noticed in the line distribution upon the films obtained for alloys above 14.3 per cent. Si and particularly for the 25 per cent. Si concentration, whether the samples are quenched from 1100° or slowly cooled after a long sojourn at 1020° to 1040° .

5. Samples of alloys containing below 14.3 per cent. Si ought to show two patterns of the same body-centered cubic type, at least when quenched from the hypothetical alpha plus gamma range. One of these patterns must belong to the higher in silicon matrix of the grain and the second, of a secondary nature, to the low-silicon alpha particles originating from the transformed gamma.

Altogether, seven alloys containing, in round numbers, 6, 8, 11, 15, 16.5, 20 and 25 per cent. Si, were exposed to the X-rays.¹⁴ For each alloy three specimens were taken—one as cast, the second as annealed for 24 hr. at 900° and slowly cooled, the third as quenched from 1000°. For two cases samples annealed at 1000° and slowly cooled were also examined.

In no case could a serious difference between the patterns of the cast, annealed and quenched samples, be detected. These tests answer the expectations listed above as follows:

1. Answer affirmative. Lattice type does not change below 14.3 per cent. Si. At 14.8 per cent. Si, faint lines belonging to a secondary constituent appear.

2. Answer affirmative. The parameters decrease, and the decrease is less strong from pure iron to a 6 per cent. silicon alloy than from 6 per cent. Si to the Fe₃Si compound.

3. Answer affirmative. The lines due to the FeSi compound are much sharper for the 25 per cent. Si alloy than for the 20 per cent. Si alloy.

4. Answer affirmative. Neither the 20 per cent. Si nor the 25 per cent. Si show any change in their patterns when the 1100° quenched and the 1020° annealed specimens are compared.

5. Answer negative. No double alpha pattern is noticeable.

This last point may be considered as a certain blow to the theory previously outlined. However, since the secondary particles also carry a considerable amount of silicon, their lattice may be so close to that of the high-silicon alpha matrix as to merge in one band instead of presenting two lines.¹⁵

DUCTILITY AND MALLEABILITY OF IRON-SILICON ALLOYS

The brittleness induced by the difference in the composition of the groundmass of each grain and the grainlets of alpha formed in the two transformations as outlined above accounts for the impossibility of cold working such alloys. Should the diffusion of silicon be a slow process, or should either voids or strains be present between the enclosed particles and the groundmass of each grain (due to unequal contraction in cooling)

¹⁴ All samples of Fe-Si alloys were ground to 150 mesh before being packed and cemented into the frames used for X-raying.

¹⁵ See appendix.

the reason for the lack of malleability displayed by these alloys would also be clear.

However, the author was able to forge all alloys below the 14.3 per cent. composition after they had been heated for 3 hr. at 1100°. They were subjected to a very slight tapping at the beginning, so as to bring about a closer contact between the delta groundmass and the enclosed alpha particles (which are now mostly in the gamma state) but not to disturb the grains too much. The range at which this forging is possible stretches from about 1050° to 1200° for the 14.3 per cent. silicon alloy and is considerably wider both ways for alloys lower in silicon; it does not, however, drop below 900° as long as the Si contact is above 6 per cent. Air-cooling or quenching when applied to the forged alloys brings about either the brushlike markings or a definite precipitate, as shown in Fig. 26. Of course, an alloy of this kind might not be expected to be ductile at lower temperatures, but a protracted 48-hr. anneal between 800° and 900° renders the forgings in an alloy with 6 per cent. silicon quite ductile and causes the alloys with 8 per cent. to become machineable (no chipping). While the author did not use much longer periods of anneal, he believes it very probable that all iron-silicon alloys up to 10 per cent. or so would become reasonably ductile by this kind of treatment, particularly in the forged state. It is of interest that alloys containing 6, 8 and 10 per cent. Si were forged by the author to a thickness of $\frac{1}{16}$ -in. This thickness did not show more than two grains, and consequently no intergranular strain ought to be caused by quenching. Still, all the water-quenched samples were extremely brittle, indicating that this brittleness is caused by structural transformations.

All chill-cast alloys above 4 per cent. silicon, particularly all quenched samples and to some extent the sand-cast ones, produce a succession of crackling sounds on cooling when the temperature drops below 600° C. Since no cracks were detected in the majority of samples the only conclusion which the author could arrive at was that these sounds were caused either by the formation of ultramicroscopic cracks due to the change of gamma particles to alpha with the corresponding dilatation, or to the breaking away of the gamma particles from the main body of each grain.

RESISTANCE TO CORROSION

It has been found by a number of investigators that iron-silicon alloys show an increased resistance to corrosion the nearer they are to the 14.5 per cent. silicon composition. This can be explained by the assumption that the compound Fe₃Si, with its 25 per cent. of atomic silicon, is most able to develop a good firm coating of SiO₂, since the atoms of silicon can not become entirely separated from one another, after the surface atoms of iron are eaten away.

It is a question as to how a further addition of silicon might affect the corrosion resistivity. There is no reason why the compound FeSi with 50 per cent. atomic silicon should be less stable chemically, toward acids at least, than Fe₃Si. Consequently there is great probability that the mixture of the two, for instance an alloy with primary crystals of Fe₃Si and a eutectic of Fe₃Si plus FeSi, could form at least as good a protective coating as the pure Fe₃Si compound. It is also possible that there might happen to be a considerable potential difference between the two compounds and this might lead to an increased corrosion. This question has never been settled experimentally and we find in the literature statements about alloys with 17 per cent. silicon being much more resistant to the action of hydrochloric acid than those with 14.5 per cent. silicon, while the latter were found on a number of occasions to be more resistant to sulfuric acid.

INFLUENCE OF ADDITIONAL ELEMENTS

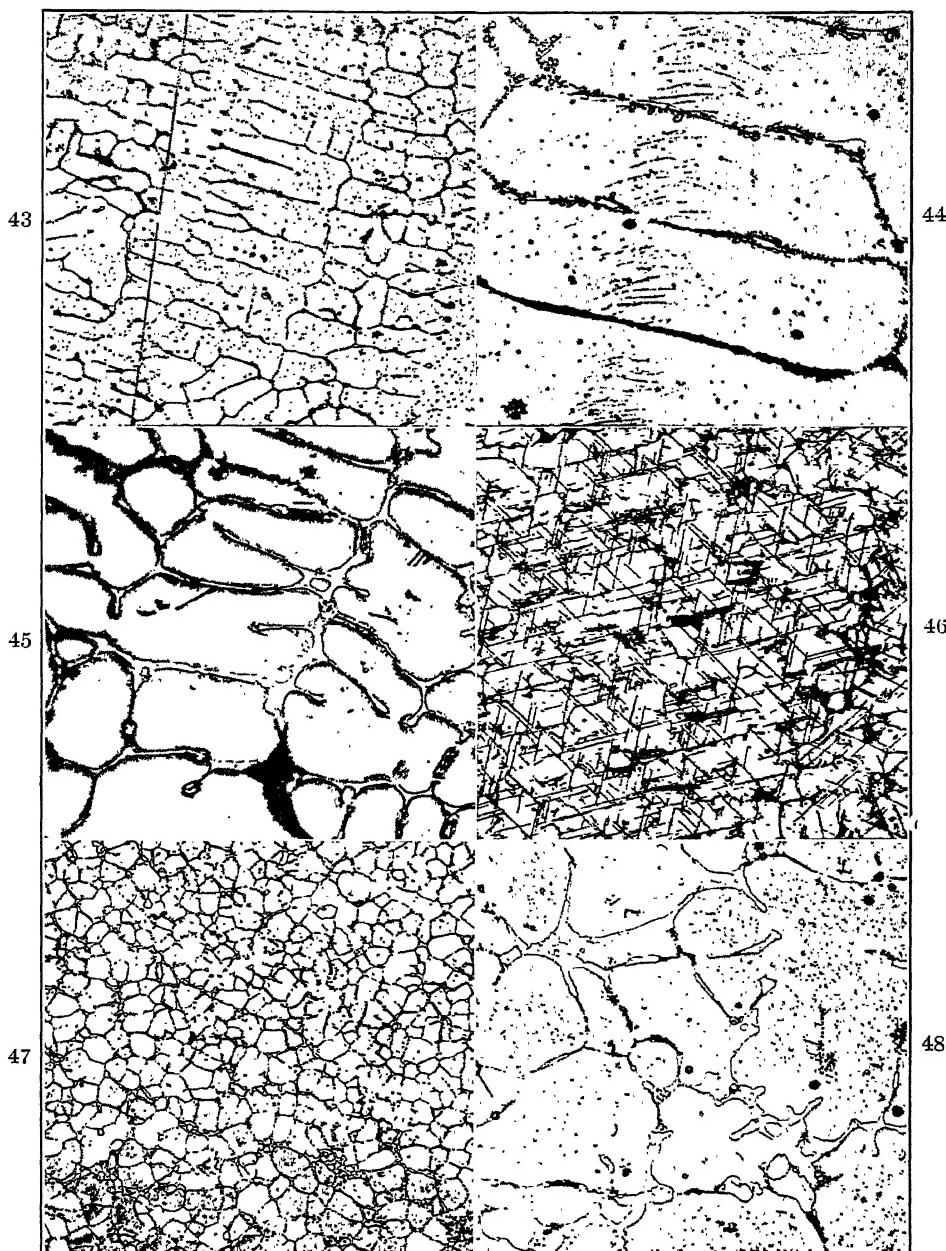
The most important of all additional elements that might be found or used in iron-silicon alloys is carbon. The usual corrosion-resistant castings are made either from the blast-furnace low-silicon pig iron or from an analogous electric-furnace product. The first may contain from 0.7 to 1.2 per cent. and the second from 0.4 to 0.7 per cent. carbon.

The question as to the influence of carbon in low-silicon alloys has been investigated by various authorities but mainly by Honda and Murakami.¹⁶ Since, at the present time, we are interested in acid-resistant alloys exclusively, only the influence of carbon upon the straight Fe₃Si compound—in other words, upon alloys where the ratio of silicon to iron is about 1:6 by weight—will be studied.

The direct introduction of carbon into a molten synthetic alloy of the Fe₃Si composition is wellnigh impossible. The author tried to introduce it by stirring the melt, covered with a fluorite flux, at a temperature anywhere between 1350° and 1500°, with either a graphitized carbon rod or a charred stick. Both burned away above the metal but remained entirely unaffected in the submerged portion. In no case did the stirring introduce more than 0.03 per cent. carbon.

It is quite possible, however, to introduce carbon by substituting some synthetically made high-carbon pig iron for a part of the iron used in the preparation of the alloy. The author used a product containing from 4.5 to 5 per cent. carbon and has been able in this way to introduce up to 0.7 per cent. carbon in a regular manner and to go occasionally up to 1.1 per cent. Usually no formation of a graphite foam would take place below 0.7 per cent. carbon but a considerable formation of the latter is always observed at higher concentrations.

¹⁶ K. Honda and T. Murakami: Structural Constitution of Iron-carbon-silicon Alloys. *Jnl. Iron Steel Inst.* (1923) **107**, 595.

FIG. 43.—HEAT 39; Fe_3Si -0.1 PER CENT. CARBON, CHILL CAST. $\times 100$.FIG. 44.—HEAT 39; Fe_3Si -0.1 PER CENT. CARBON, CHILL CAST. $\times 500$.FIG. 45.—HEAT 40; 14.9 PER CENT. Si-0.25 PER CENT. CARBON, CHILL CAST. $\times 500$.FIG. 46.—HEAT 40; 14.9 PER CENT. Si-0.25 PER CENT. CARBON, SAND CAST. $\times 100$.FIG. 47.—HEAT 41; 15.1 PER CENT. Si-0.41 PER CENT. CARBON, CHILL CAST. $\times 100$.FIG. 48.—HEAT 41; 15.1 PER CENT. Si-0.41 PER CENT. CARBON, CHILL CAST. $\times 500$.

The shape in which carbon might be present in the Fe₃Si alloy cannot be defined in the simple manner that is used in the discussion of the relative behavior of carbon and silicon in steel and cast iron. To begin with, there may be a formation of iron carbide, Fe₃C in the liquid state. This iron carbide might crystallize separately or isomorphically with the Fe₃Si compound. Again, it might dissociate in the melt into graphite, this graphite crystallizing eutectically; or the graphite might be formed from the individual carbide or the isomorphic crystals of Fe₃Si plus Fe₃C at some lower temperature.

Figs. 43 and 44 show the structure of a chill-cast alloy containing about 14.5 per cent. silicon and 0.1 per cent. carbon (synthetically introduced). At a magnification of 500, the intercrysalline patches of the FeSi compound which formed from the excessive silicon can be seen. In some spots, this FeSi compound is covered with a black film, probably of graphite. In others there are round grayish particles, which can be scarcely anything else but iron carbide.

Fig. 45 shows the structure of a chill-cast alloy containing 14.9 per cent. silicon and 0.25 per cent. carbon. There is a considerable excess of the FeSi compound but nowhere do we find a sign of a definite presence of either iron carbide or graphite.

A part of the same melt yielded an entirely different structure when sand cast. In Fig. 46, we see no definite grain boundaries but the whole mass of the alloy is traversed by a parallel striation of dark lines running in three main directions. The conclusion seems evident that in this case graphite has been precipitated from isomorphous crystals along the octahedral cleavage planes.

Figs. 47 and 48 show the microstructures of a chill-cast alloy with 15 per cent. silicon and 0.4 per cent. carbon. Again, there are large patches of FeSi between the grains of Fe₃Si and in addition a small number of black dots of graphite; too small to account for the total carbon. No definite presence of particles of carbide is noticeable.

Figs. 49 and 50 represent the structure of a chill-cast alloy with 0.6 per cent. carbon and 15.2 per cent. silicon and here we see a considerable amount of film and dots of carbon; not enough, however, to account for the total amount of carbon present.

A part of the same melt was poured into a hot bronze mold, and because the chilling effect was not so strong a very fine eutectic of graphite resulted (Fig. 51). The difference in appearance between Figs. 49 and 51 (transverse test bars of identical dimension and obtained from the same melt, but at different rates of cooling), is rather appalling.

When cast in dry sand, the same melt (with 0.60 carbon) seems to have its whole carbon content crystallized in the form of a very rough eutectic in which the films of graphite have the same appearance as in gray iron.

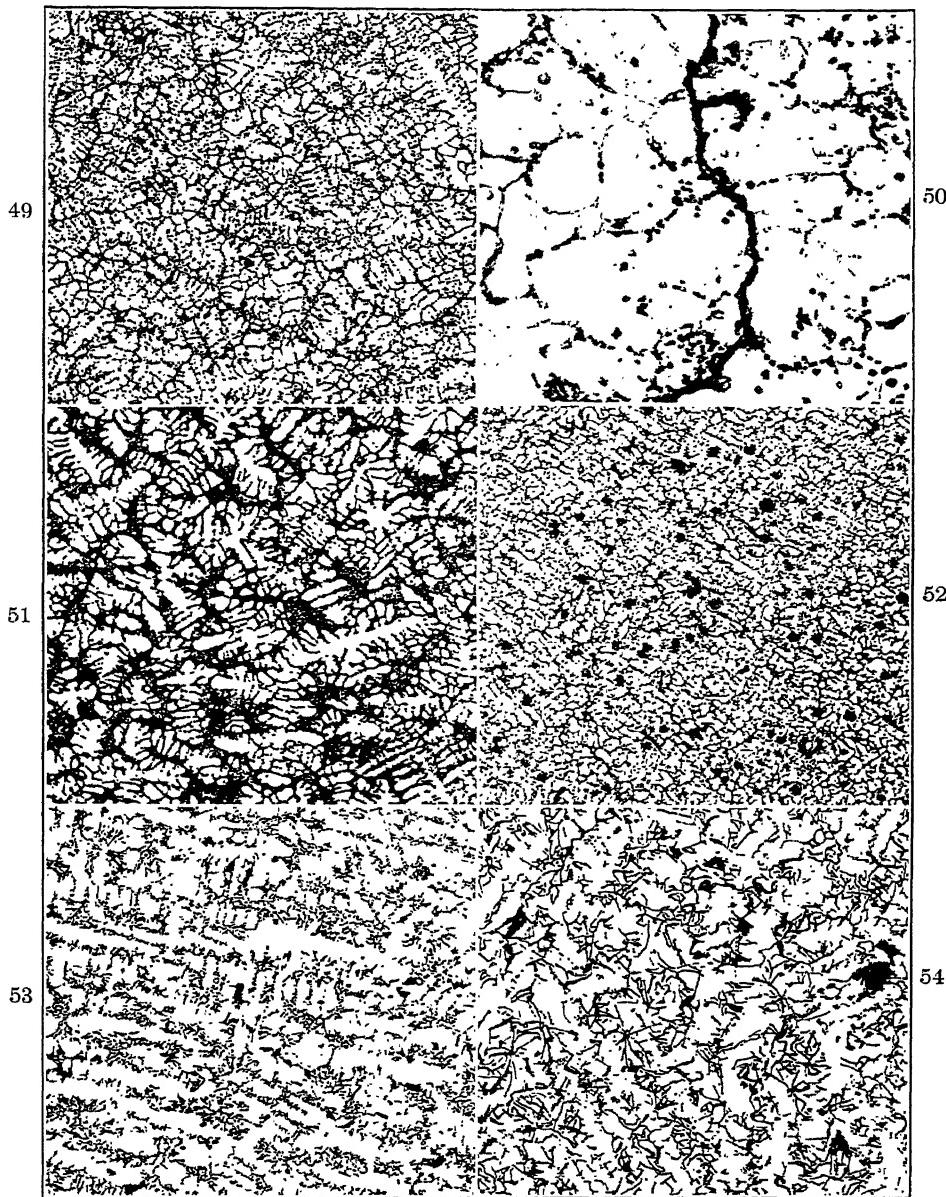


FIG. 49.—HEAT 42; 15.2 PER CENT. SI-0.60 PER CENT. CARBON, CHILL CAST. $\times 100$.

FIG. 50.—HEAT 42; 15.2 PER CENT. SI-0.60 PER CENT. CARBON, CHILL CAST. $\times 500$.

FIG. 51.—HEAT 42; 15.2 PER CENT. SI-0.60 PER CENT. CARBON, CAST IN A BRONZE MOLD. $\times 100$.

FIG. 52.—HEAT 46a; 15.2 PER CENT. SI BLAST-FURNACE IRON REMELTED, CHILL CAST AT A VERY LOW TEMPERATURE. $\times 100$.

FIG. 53.—HEAT 46b; SAME AS 52 BUT SAND CAST, EDGE OF BAR. $\times 100$.

FIG. 54.—HEAT 46b: SAME AS 53 BUT SAND CAST, CORE OF BAR. $\times 100$.

It is interesting to note how the presence of carbon influences the hardness, transverse strength and the electric resistivity of the 14.3 per cent. silicon alloy. Since it is very difficult to maintain an exact concentration of silicon in experimental melts, the results of these tests may not be sufficiently regular to permit the plotting of diagrams and the establishing of some specific laws, but it was found that neither the synthetic nor the Fe₃Si plus carbon alloys, nor the usual carbon-bearing foundry products, can show the same minimum of electric resistivity as corresponds to the binary alloys with 14.3 per cent. silicon. Instead of 37 microhms for the synthetic Fe₃Si alloy we find at least 54 microhms for 0.1 per cent. carbon, and 67 for 0.25 per cent. Beyond this point the amount of carbon does not affect the resistivity.



FIG. 55.—HEAT 48; SAME AS 52 BUT SAND CAST AT A TEMPERATURE 150° HIGHER.
X 100.

The hardness of the alloys drops in the presence of carbon, particularly so in sand-cast specimens, and with 0.35 per cent. one obtains sometimes a hardness of 36 Rockwell instead of 52 for the pure binary alloy. In the chill-cast state, however, the hardness remains high, never dropping below 50 Rockwell and sometimes going up to 55.

The presence of carbon has a definitely beneficial influence on the strength of the synthetic alloys, provided its content is above 0.35 per cent. With less than 0.2 per cent. the breaking strengths of the pure and the carbon-contaminated alloys are really identical, while at 0.65 per cent. carbon content there is a considerable difference in the strengths of the chill-cast and sand-cast test bars. The eutectic in the chill-cast bars is fine and evenly distributed, therefore probably is in a more intimate contact with the total mass of the metal; consequently strengths from 50 to 70 per cent. higher are obtainable with the use of chills.

A low-temperature anneal, not exceeding 600° C., increases the strength of both the sand-cast and chill-cast test bars and in a



56

57

58

FIG. 56.—COMMERCIAL DURIIRON SAND CAST. UNETCHED. $\times 100$.

FIG. 57.—COMMERCIAL DURIIRON SAND CAST. ETCHED. $\times 100$.

FIG. 58.—COMMERCIAL DURIIRON SAND CAST. ETCHED. $\times 500$.

59

60

61

FIG. 59.—COMMERCIAL DURIIRON CHILL CAST. UNETCHED. $\times 100$.FIG. 60.—COMMERCIAL DURIIRON CHILL CAST. MODERATE CHILL. ETCHED. $\times 100$.FIG. 61.—COMMERCIAL DURIIRON CHILL CAST. STRONG CHILL. ETCHED. $\times 100$.

few of the chill-cast bars breaking strengths as high as 1400 lb. were found.

There seems to be, however, a certain even more subtle influence which makes the higher figures rather erratic, and consequently for samples annealed at 600° C. the figures of 950 lb. for chill-cast bars and 750 lb. for sand-cast bars must be accepted. This would correspond approximately to 45,000 and 36,000 lb. respectively for the extreme fiber stress.

Our next study dealt with the properties and structures of alloys obtained by remelting and refining the blast-furnace product. Figs. 52-55 show the structures of a plain 15 per cent. blast-furnace iron-silicon

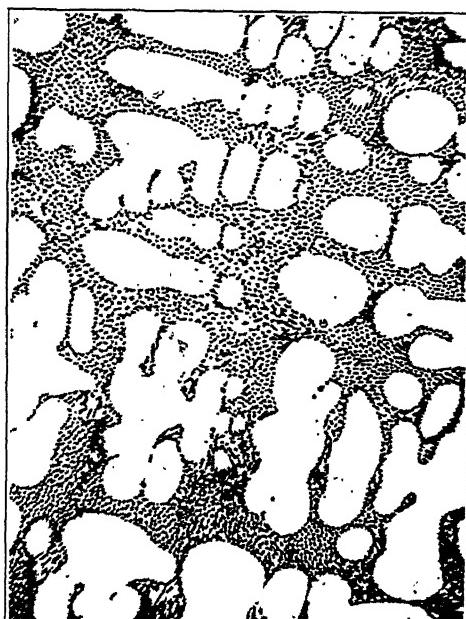


FIG. 62.—COMMERCIAL DURIIRON CHILL CAST. MODERATE CHILL. ETCHED. $\times 500$.

remelted and cast in chills and in sand molds. The product contained 0.8 per cent. Mn and 0.15 per cent. phosphorus in addition to 0.70 carbon. None of the secondary components shows up in the photomicrographs, which represent mainly and in a consecutive manner the influence of the rate of cooling upon the fineness of the Fe₃Si plus graphite eutectics. In the chill-cast state (Fig. 52) it is again very fine, while in the sand-cast state, as obtained by casting at 1400° C., it is quite rough (Fig. 55).

The usual practice in making corrosion-resistant Fe-Si castings is to remelt the blast-furnace product and add to it either some pig iron or electric-furnace ferrosilicon, to bring its composition to the desired one of 14.5 per cent. silicon plus 0.8 per cent. carbon, the product is shown by Figs. 56 to 62, which reproduce the structures of the usual "Duriron"

as cast either in sand molds or with the addition of chills. In Fig. 56 (unetched) can be seen the roughness of the intergranular flakes of graphite in bars obtained by sand casting, while in Fig. 59 (also unetched), corresponding to the chill-cast bars, there is much less primary graphite and it is in much finer shape. Other photomicrographs in this series present the same samples as etched. The sand-cast bars show primary graphite, primary Fe_3Si and a large field of a grayish eutectic. In the chill-cast state, no primary graphite is observed; the eutectic is much more evenly distributed and seems to be much darker. The islands of Fe_3Si are also much smaller and more evenly distributed. At high mag-



FIG. 63.—STRUCTURE OF A 14.5 PER CENT. SI ALLOY WHICH HAS BEEN REMELTED IN A ROSS-TACONY CARBORUNDUM CRUCIBLE. X 100.

nifications, as shown in Figs. 58 and 62, the difference of the shapes of the graphite in the sand-cast and the chill-cast samples resembles closely the different shapes of silicon in the plain and the modified aluminum-silicon alloys.

The temperature of pouring seemed to affect the strength and the hardness of the carbon containing alloys quite considerably. Bars cast at a temperature of 1300° C. have shown much more strength than those cast at the higher temperatures.

CONCLUSIONS CONCERNING THE NATURE OF $\text{Fe}_3\text{Si} + \text{C}$ ALLOYS

On the basis of microstructural examination and electric-resistivity data, the author believes it possible to establish the following conception of the pseudobinary $\text{Fe}_3\text{Si} + \text{C}$ series.

The $\text{Fe}_3\text{Si} + \text{C}$ system is a eutecticiferous series. The eutectic is located about 1.1 ± 1 per cent. Si. From the ease of casting at considerably lower temperatures than are required for the straight Fe_2Si composition, the eutectic point may be placed about 1200° C.

With a little more than 1.1 per cent. carbon the system enters the region of incomplete miscibility; *i. e.*, the melt is built up of two layers—a liquid composed of Fe_3Si plus 1.1 per cent. and a foam of graphite.

Primary crystals separating from a hypoeutectic melt do not represent the pure Fe₃Si compound but contain carbon to the maximum amount 0.40 to 0.45 per cent. This carbon probably is not in the form of carbide which might be compelled to crystallize isomorphically with Fe₃Si, but is present as an absorbent. It increases the electric resistivity and decreases the hardness of the alloy.

The limit of the solubility of carbon in Fe₃Si drops considerably with the temperature. These cooling velocities that are proper to a greensand mold suffice to throw out of solid solution a considerable amount of the excess carbon and to allow the latter to grow into large flakes.

Chill-cast alloys appear to retain a considerable amount of carbon in solid solution. Since, however, their electric resistivity does not increase beyond the point obtainable with 0.2 per cent. carbon and since the resistivities of the sand-cast and chill-cast samples are nearly equal, it must be granted that hardly as much as 0.2 per cent. and probably not more than 0.15 per cent. carbon can be retained in solid solution under any conditions.

When the carbon content is small, it lacks the ability to grow into flakes or visible particles of any kind but is precipitated at the octahedral planes and separates the grains into layers, completely ruining their strength.

The same thing happens when carbon is introduced in the form of silicon carbide. In a case where a pure Fe₂Si was remelted incidentally in a Ross Tacony crucible it absorbed 0.2 per cent. carbon in the cast state and developed a very brittle loose structure as shown in Fig. 63.

Alloys higher in carbon than 0.4 per cent. must consequently contain two kinds of graphite—the eutectically crystallized and the one that has been precipitated from the solid solution. The first probably acts as centers of growth and absorbs the precipitated graphite, forming either globules (chill-cast state) or flakes (sand-cast).

The mechanical influence of carbon is indicated in Table 1.

TABLE 1.—*Influence of Carbon in Fe₃Si Base-alloy Casting*

Carbon below, Per Cent.	Chill Cast, Annealed at 600° C.		Sand Cast, Annealed at 600° C.
	Brittleness	Extreme Fiber Stress, Pounds	Extreme Fiber Stress, Pounds
0.03	Very brittle		About 20,000
0.10	Less brittle	10,000	About 11,000
0.25		15,000	About 8,000
0.45		29,000	About 24,000
0.65		36,000	About 27,500
0.80		43,000	About 32,000

INFLUENCE OF OTHER METALLIC AND NON-METALLIC ADDITIONS

We were interested also to know if the mechanical properties of the Fe_3Si base-alloy castings might not be considerably improved by a suitable addition of some other element. Two compositions were chosen as basic ones to be alloyed with other elements; one with silicon constant at 14.3 per cent., carbon below 0.3 per cent. and the iron replaced by some other element; another with silicon kept at the same level, but the carbon

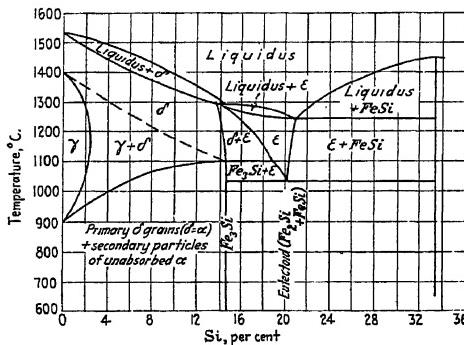


FIG. 64.—VARIATION OF DIAGRAM SHOWN IN FIG. 10.

content amounting to 0.7 per cent. Four elements were tried out as substitutes for iron, namely: chromium, 2 to 16 per cent.; vanadium, 0.5 to 3 per cent.; manganese, 0.5 to 3 per cent.; nickel, 2 to 6 per cent. Two others—boron, 0.3 to 1 per cent. and aluminum, 0.5 to 1 per cent.—were tested as to their general (scavenging and alloying) influence.

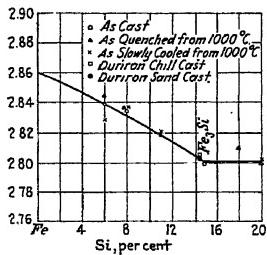
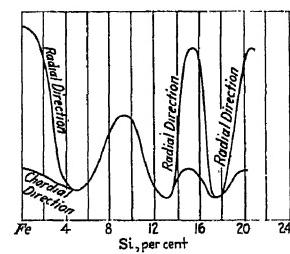


FIG. 65.—PARAMETERS OF THE CUBIC LATTICE OF Fe-Si ALLOYS.
FIG. 66.—RELATIVE SIZES OF GRAINS OF SAND-CAST ROUND BARS.



It must be remembered that all experiments in this series were made before the author had established the actual nature of the acid-resistant Fe_3Si . At that time, he still regarded these alloys as nothing else but members of a limited solid-solution range of silicon in iron, probably stretching up to 20 per cent. silicon. From the standpoint of this conception it was consistent to assume that some element might soften the alloys either by eliminating some "contamination" or by lessening the

distortion of the crystalline lattice. None of the experiments resulted in a highly positive improvement, while most of them yielded alloys of an inferior quality.

Table 2 shows how the breaking strength and hardness changed due to various additions. One sees that with the exception of manganese and nickel, which always produce some softening, and of vanadium, which produces a somewhat increased strength, these additions either had no action or made the alloys inferior. Manganese and aluminum were particularly bad in their effect upon the breaking strength.

These poor results of substitution alloys could be foreseen from the viewpoint established above; namely, that all acid-resistant alloys of the iron-silicon series represent mainly the Fe_3Si compound plus a small amount of FeSi and some graphite in a variable state of distribution. It explains why all efforts to improve these with the aid of additional elements are doomed to be negative. Suppose, for instance, that we have a straight Fe_3Si composition and substitute some other element for a part of the iron. In the case of nickel and manganese, which do not form compounds of the same type (neither Ni_3Si nor Mn_3Si exist) and which do not show such strong ability as iron to keep silicon in solid solution, the following situations might ensue:

1. The additional metal will take away part of the silicon from iron and a mixture of the compound Fe_3Si plus the compound Ni_2Si or Mn_2Si is obtained. In fact, we will not obtain a mixture of Fe_3Si and Ni_2Si either by an atomic or gravimetric substitution of nickel for iron. The compound Ni_2Si draws a considerably larger amount of silicon than Ni_3Si would do. Consequently we might obtain a mixture of (Fe_3Si plus Fe) plus Ni_2Si . Quite logically this mixture may not have any better strength or a much lower hardness than the plain Fe_3Si alloy.

2. Should it happen, however, that nickel will not take away silicon from iron, a substitution of nickel for iron (with the amount of silicon kept at the same level) would result in upsetting the Fe:Si ratio required for the formation of Fe_3Si and the excess of silicon would form an excess of the compound FeSi . A rather small excess of silicon so formed would tend to develop a considerable amount of FeSi . Nickel itself would have either to remain separately as a third strictly metallic phase or to be absorbed by one of the compounds. Since the compound FeSi displays a very sharp composition while the Fe_3Si shows a tendency to form absorption products with iron, nickel might be expected to go into the crystals of Fe_3Si . We know, however, that alloys possessing slightly less than 14.3 per cent. of silicon are by no means less brittle and definitely less corrosion-resistant than the Fe_3Si composition. When either nickel or manganese is absorbed by the Fe_3Si compound they might be expected also to contribute to the formation and a partial preservation of the gamma solid solution. In fact, with alloys containing 14.5 per cent. sili-

con and from 2 to 4 per cent. nickel or 1 to 2 per cent. manganese, the brushlike markings, which are characteristic of binary alloys of much lower silicon contents only reappeared (in spots, at least). These conditions do not tend toward improvement in strength or resistance to corrosion.

On the other hand, a decidedly positive effect of nickel additions amounting to 0.3 to 0.5 per cent. has been found in the forging tests. While of six 2 by 1 in. ingots (cast in 800° C. hot alumite mold) of the

TABLE 2.—Physical Properties of Iron-silicon Alloys

Number of Heat	Per Cent. Silicon	Per Cent. Addition	Rockwell "C" Number	Cantilever Strength ^a			Electric Resistivity (Microhms per Cubic Centimeter)								
				Chill Cast	Sand Cast	Sand Cast Annealed	Chill Cast	Sand Cast	Annealed ^b	Quenched ^c	Chill Cast	Sand Cast	Annealed ^b	Forged Annealed ^b	Forged Quenched ^c
37	2.6			24	23	23	650	1,050	>2,000	>2,000	52	41		42.4	42.3
38	4.0			27	26	25	350	750	2,100	1,600	55	52	53	54	53
73	5.0			32	34	31	320	650	1,900	900	71	69	70		
2	6.26			32	33	31	220	580	1,300	350	82				
23	5.9			33	33	31	300	570	1,500	275		81	84		
24	6.1			39	38	27	150		650	200	80.5		81		
3	8.6			39			170	600	700	150		113			
21	7.7			40	41		450		1,350	150		87.5	90		
22	7.9				120		120		1,500	150	88		89		
74	9.0				80		475		1,020			98	96		
66	10.3						380		900			98.1	92		
20	11.1						275		200		106	100	103		
75	13.3						220		500			66	67.5		
29	14.6						350		460			50.5	42		
30	14.75			53.5	50		50		520						
33	15.1						170		1,500						
7	20.00			53	50		20		170		107	111			
85	14.3	0.4 V?			48		420		480			58			
36	14.3	2.7 V?			50		300					82			
43	14.3	0.6 Mn?			46		350		250			61	59		
44	14.3	1.5 Mn?			45		250		250			69.5	69.0		
45	14.3	3.0 Mn?			46		350		380			67.0	64.5		
53	14.3	2.0 Ni?			47		300								
54	14.3	6.0 Ni?			49		350								
69	14.3	2.0 Cr?			51		200								
71	14.3	16.0 Cr?			52		320		460						
63	14.3	0.5 Al?			49		280				112				
61	14.3	1.0 Al?			48		300								
86	14.3	0.3 B?			47		340								
87	14.3	0.7 B?			46		320								
39	14.3	0.12 C			43		150	{ 270 } { 220 }	235		59	87.5			
40	14.3	0.25 C		56	36		220	{ 270 } { 310 }	175		72	209			
42	14.3	0.60 C		50	44		600	{ 500 } { 750 }	560	560	67.3	70			
14	14.3	0.95 C					430	{ 650 } { 480 }							
46	15.1	0.55 C		50	39		400	{ 420 }							
51	14.5	0.75 C					400		380		89	90.5			
58	14.5	2.0 V?					350		430		97	98			
64	14.5	0.75 C					300		280						
65	14.5	0.5 Al?					350		370						
55	14.5	0.75 C					300		250						
72	14.5	8.0 Cr?					420		480						
	14.5	0.75 C													
	14.5	16.0 Cr?													

^a Expressed in pounds of load applied to 0.5-in. square bar with lever 1 in. long.

^b Annealed either at 900° or 1000° C. followed by slow cooling. Usually the highest figure is given.

^c Quenched usually at 950° C., in a few cases, at 1000° or 1050°.

strict Fe_3Si composition, only two could be reduced by 50 per cent. without complete cracking, five out of six ingots containing 0.5 per cent. Ni were forgeable.

Vanadium and chromium, being much more active elements than iron, are more likely to form silicides even at the expense of iron, and at least chromium is definitely known to form a silicide of the formula Cr_3Si . Frilley¹⁷ determined the Cr_3Si from specific density tests, and the author recorded microscopically a definitely single phase in a Cr-Si alloy when the silicon content amounted to 15.5 per cent. Quite logically, a silicide of this formula might be rather apt to crystallize isomorphously with Fe_3Si , and the author actually found that in the presence of quite large quantities of vanadium or chromium, no additional constituent was formed, the result being probably the formation of a mixed silicide. Again, the mixed silicide, being an intermetallic compound, can not be expected to be much stronger than the plain Fe_3Si . In fact, the author found, as shown in Table 2, a moderate but definite improvement in strength always caused by the presence of vanadium, while no improvement was caused by chromium.

Vanadium had a decidedly advantageous influence in forging tests to which *low-carbon* Fe₃Si base alloys (about 0.3 per cent. carbon) were subjected. Plain alloys with 14.5 per cent. silicon and 0.2 per cent. carbon did not forge at all, while those containing 1 per cent. vanadium forged in three cases out of eight.

A poor feature of the three metals, vanadium, chromium and manganese, is their tendency to discolor the surface of the casting. As little as 0.5 per cent. vanadium produces a dirty blue; 3 per cent. chromium makes the surface greenish and wavy; 2 per cent. manganese produces a uniform brownish coating.

When boron is used as a substitute for iron, there is hardly a chance for the formation of a boron silicide, while the appearance of an iron boride is more or less probable. A substitution of boron for iron causes the alloy to contain less iron than required to form the Fe_3Si compound, to say nothing about the necessity of saturating the affinity of the added boron. Consequently iron is compelled to form a considerable amount of FeSi and some boride in addition to some Fe_3Si . The boride may crystallize isomorphously with Fe₃Si while FeSi will most probably remain as a separate phase. This has been corroborated by a microscopic examination of the boron-containing alloys. They have always shown an increased amount of FeSi between the grains of the basic alloy, but no third constituent traceable to boron has been detected. Again neither a mixture of a mixed silico-boride with FeSi nor a more complicated mixture of silicides and borides stands a chance to be more reliable

¹⁷ *Rev. de Mét.* (1911) 8, 457-558.

mechanically or chemically than the plain Fe_3Si compound, and our tests proved this contention quite definitely. This in spite of the fact that additions of boron to acid-resistant iron-silicon alloys form the subject of certain patents.

As far as the substitution of aluminum for iron goes, the author found the results to be exceptionally bad. All alloy samples were impregnated with films of aluminum oxide and this was true both for the synthetic binary alloy and for the one containing 0.7 per cent. carbon. In no case was even the slightest improvement in mechanical properties noticed, while most of the test bars broke under low loads. The microscopic examination did not reveal the presence of a separate constituent, only the amount of FeSi increased in the same manner as it did in the case of boron. Again, a mixture of FeSi with films of aluminum oxide, when located at the grain boundaries of a double silico-aluminide of iron can by no means be considered as a strengthening medium, so the poor results obtained with the addition of aluminum become explainable.

The effect of aluminum upon the surface of the castings was also rather bad. It produced a dull gray shade and robbed the surface of that smoothness so characteristic of the strictly binary FeSi alloys and of the industrial Duriron.

In the case of the ternary industrial alloys containing iron, silicon and carbon, as the main components, the introduction of additional elements named above was not found to be more conducive to better results, only a slight variation being introduced due to the presence of carbon.

Relation of Additional Element to Carbon

Disregarding the previously discussed reactions of the Fe_3Si compounds with the additional elements, we will have to consider only the relationships of the additional element to carbon. Elements like nickel and manganese do not have any particular affinity to carbon; consequently they did not affect the structure of the usual "Duriron" type of alloys, except to introduce spots of the brushlike markings. Chromium and vanadium are known to have a strong affinity to carbon and in their presence a third constitutional element—a carbide of vanadium or chromium—is formed. This carbide lies within the eutectic patches and decreases consequently the amount of the eutectic graphite present. We have seen, however, that the eutectic graphite has a cushioning effect. It prevents the alloys from chipping in the grinding process and prevents also the concentration of shocks at the stricken spot. Accordingly, the lowering of its amount by the formation of a carbide of vanadium or chromium may not and actually does not increase the strength of the alloy. Again, as with the binary alloys, when a part of the iron is replaced by one of these two elements they display also a tendency to

form a silicide, which in its turn crystallizes isomorphously with Fe_3Si . Accordingly, we see that both chromium and vanadium must take part both in the formation of a double silicide and of a carbide according to some law of distribution. The author found the amount of carbide formed per unit of vanadium considerably higher than that formed per unit of chromium. This seemingly indicated that chromium has a stronger tendency than vanadium to form a silicide and stay with the Fe_3Si . Even with 16 per cent. chromium, an alloy containing 0.8 per cent. carbon did not become more than half degraphitized, which indicates according to the formula Cr_3C_2 , that only 2.6 per cent. chromium will combine with carbon while 13.4 per cent. remains with the iron silicide.

ACKNOWLEDGMENTS

The writer wishes to thank Peirce D. Schenck, president The Duriron Co., Inc., for the generous support he gave the author in this investigation and for permission to publish the results; J. H. Critchett, vice president, Union Carbide and Carbon Research Laboratories, Inc., for the assistance rendered the writer by the laboratories; and J. R. Vilella and E. C. Bain of the Union Carbide and Carbon Research Laboratories, Inc., the former for his help in etching and photographing a great number of samples described, and the latter for making the X-ray diagrams and calculating the parameters.

APPENDIX 1

E. C. Bain, of the Union Carbide and Carbon Research Laboratories, Inc., recently calculated the actual parameters of the lattices of iron-silicon alloys. It has been found that the parameter decreases from 2.86 Ångstroms for pure electrolytic iron to 2.80 for the Fe_3Si compound. Beyond 14.8 per cent. Si by analysis, additional lines were found, those corresponding, however, to a body-centered cube and having the same parameter with Fe_3Si averaging 2.802 Ångstroms. Quenching and annealing had little effect on the length of the parameter with the exception of alloys containing 6 per cent. Si. With these alloys the quenched specimen had a parameter of 2.845 and the annealed 2.829. The change in parameters is shown in Fig. 65.

APPENDIX 2

Macrostructural Features of Iron-silicon Alloys as Sand Cast.—The author is of the opinion that the type of visible crystallization is very much affected by the processes which take place within the original grain after solidification. He is not ready to establish a definite theory and consequently wishes to present here only a few of his observations. Since chill casting retards considerably every process taking part on solidifica-

tion, all observations had to be made upon sand-cast bars of various diameters from $\frac{1}{2}$ to 3 inches.

A. Pure iron crystallizes in long columnar grains frequently reaching into the very core of the bar.

B. At about 2 per cent. silicon the number of equiaxed crystals of the core increases and at from 4 to 6 per cent. Si the grains are very uniform, both as to shape and size.

C. At from 9 to 10 per cent. Si the bars are built up of uniformly equiaxed, quite large grains which form sharply separate annular layers.

D. Beyond 10 per cent. Si the grain size again decreases and becomes almost microcrystalline at about 13 per cent. Si.

E. At about 14.5 per cent. Si (± 0.5 per cent.) there are again long columnar grains similar to those of a pure metal.

F. Beyond 15 per cent. Si the structure again becomes microcrystalline. On further increase in the amount of silicon a conchoidal fracture is obtained. However, the etched cross-section of alloys approximating the eutectic composition again shows a beautiful columnar crystallization like that of a pure metal. The only difference is that the grains are now opalescent and iridescent.

G. Beyond 20 per cent. Si the macrostructure again becomes blurred.

The tendency of the change in grain dimensions is shown qualitatively in Fig. 66.

APPENDIX 3

The following materials were used in making the experimental melts:

Iron.—Regular Armco iron.

Silicon.—(1) 97.8 per cent. silicon electric furnace product. (2) In a few instances, 50 per cent. electric furnace FeSi. (3) Blast-furnace product with 15 per cent. Si and 0.8 per cent. C.

Chromium.—98 per cent. electric furnace chromium.

Vanadium.—40 per cent. electric furnace ferro-vanadium low in carbon.

Nickel.—Electrolytic.

Manganese.—97 per cent. electric furnace product.

Carbon.—4.5 per cent. carbon synthetic chill-cast iron.

Boron.—20 per cent. ferroboron (German product).

DISCUSSION

P. A. E. ARMSTRONG, New York, N. Y.—This is an extremely interesting paper to me. The brittleness of solid solutions of iron and silicon is a regrettable accompaniment of this wonderful alloy. Apparently silicon is readily dissolvable in iron and exists primarily as a solid solution in iron up to about 20 per cent. I firmly believe that silicon is dissolved in iron by first forming a definite chemical compound of silicon and iron, which in turn is dissolved in the molten iron. On cooling there is presumably a strong tendency for the solid solution to liberate chemical compounds

of perhaps ultramicroscopic size. Whether or not this is partly an explanation of the electric-resistivity curve shown on page 259 of the paper is a matter of speculation on my part. To me increasing quantities of a definite chemical compound are liberated by the mother metal from the liquid to the cooling condition and these ultramicroscopic compounds are found along the grain boundary and the crystal planes, which partly accounts for the increasing electrical resistance. The crystal itself being higher in its silicon component also accounts for the increasing electrical resistance. These two factors appear to go hand in glove with one another and there is a rapid falling off in electrical resistance, which reaches its maximum at about 14.5 per cent. silicon coinciding with the formula Fe_3Si , thereafter the mixture results in a rapidly increasing resistance as the percentage of silicon goes up. The brittleness, which is such a great trouble to metallurgists who are concerned with the mechanical properties of these alloys, is perhaps partly due to the liberation of microscopic and ultramicroscopic silicon-iron compounds. My belief in this is strengthened by my experience, which has taught me that high-silicon irons, even with other elements, in solution have great weakness at their crystal boundaries and along their cleavage planes. The fractures, as I have noticed them, have usually broken along the crystal boundary or a well marked cleavage plane. I do not recall seeing any fracture of high-silicon irons or alloy irons that did not show this characteristic fracture. It could be assumed that silicon-iron alloys should be heated and quickly quenched, so as to hold the separated compound in solution. Quenching such alloys does not increase their strength. From this I assume, as there is practically no change in the type of fracture, that it is impossible to put back in solution the compounds which have separated and have resulted in this characteristic brittleness. Unfortunately many of the metallic silicon compounds have about the same brittleness as the iron-silicon compound. An interesting exception is nickel, which will carry a very large amount of silicon in the mother metal and still produce a tough alloy. For instance, an alloy containing 20 per cent. of nickel, 9 per cent. of silicon and the remainder iron, is quite tough at atmospheric temperatures and brittle when heated to about 1000° F. or higher. Unfortunately the nickel changes the acid resistance of the alloy and unfits it for some purposes where the ferrous alloy minus nickel would be particularly suitable.

M. G. CORSON.—The decrease in the electrical resistance which takes place from 10 per cent. to 14.4 per cent. silicon is strictly in agreement with the mechanical state. Is a compound an ingredient? Then it must have a definite facility. In a system of this kind, we have a number of compounds between FeSi and FeSi_2 . Compounds are usually according to medium and maximum curve. The FeSi is occupied by a maximum. We would not be able to electrify this compound. It might be simply a case of one solid solution. So the presence of one maximum in the diagram immediately calls for the presence of a medium in the mechanical compound.

The form of straight lines has been brought out. My idea is that when the delta transforms into a delta grain a number of particles of gamma contact and it is quite possible that the resultant particles are not as definitely in touch with the contours of the grain. So instead of having the straight effect, as usual when the compound is precipitated, we have a weakening, because the alloys are changed.

S. L. HOYT, Schenectady, N. Y.—It seems that there are a few points that should not be allowed to pass without comment. For instance, the author passes from delta to gamma plus delta and alpha plus delta on cooling, giving an impossible construction to his diagram.

For instance, gamma plus delta is supposed to change to alpha plus delta. At the transformation point, there must be three phases in equilibrium: gamma, delta, and alpha. This would occur at only one temperature, and yet the line is drawn so as to

indicate that this equilibrium takes place over a range of temperature. How would the author reconcile such a situation?

Secondly, the heterogeneous field is indicated as alpha plus delta. The interpretation of the physical properties, electrical conductivity, etc., would require a simple homogeneous field of alpha. The author attempts to show that this is a two-phase field by the microstructure and particularly by the presence of the barley grain constituent. Now if that be, indeed, a second constituent, which I seriously doubt, we would expect to find that it increases from zero up to 100 per cent. at the composition of the second phase. I believe the author does not show that to be the case.

On the other hand, it seems that the alloys along the middle of this range are those which show this peculiar structural constituent most fully developed, and that the relative amounts of these two phases are altered by means of a thermal treatment. It seems to me that these two considerations would require us to dismiss the concept which the author advances.

I consider this a very valuable contribution to our knowledge of the iron and silicon alloys, and these remarks are meant to apply more to the author's interpretation of the data given, and not to the data proper, with the exception of the barley constituent. I am sure if I had occasion to look up literature on this system, Mr. Corson's paper would be one of the first to which I would turn.

R. HAY, Glasgow, Scotland.—Mr. Corson's paper forms a very acceptable addition to our knowledge of the iron-silicon system and has the commendable feature of dealing with the subject from many sides. The constitution of the iron-silicon alloys has received much attention in recent years and the present paper shows that the last word has not yet been said on this subject. In 1926, Phragmén published a paper¹⁸ in which he gives the equilibrium diagram of this system based upon previously published work and upon his own X-ray investigations. His diagram differs considerably from that given in the present paper. Phragmén shows the limit of the gamma range occurring at about 3 per cent. silicon. Beyond this, to about 15 per cent. Si, there exists only one phase alpha (or delta) from the solidus to room temperature. In one other important respect this diagram differs from that of the author; namely, Phragmén shows a marked decrease of solubility of the compound of iron and silicon (theta) in the alpha phase with decrease of temperature.

It would appear, however, to be proved beyond doubt by the photomicrographs of the author that the gamma phase does extend beyond 3 per cent. Si although the evidence for extending it to 14.3 per cent. Si seems to the writer to lack sure foundation. On page 265 it is stated, "In a sample (6 per cent. Si alloy) chill cast and annealed for a long time at 950° C., with a particularly long cooling period between 900° and 800° C., the markings disappeared completely and the alloy looked more or less like the one with 4 per cent. Si, shown in Fig. 14." Was the 4 per cent. Si alloy definitely duplex in structure? The photomicrograph does not show this distinctly but it is often difficult to obtain a clear photograph of a very fine duplex structure. Again, on page 266 the author would appear to suggest that prolonged soaking at a high temperature followed by slow cooling appears to eliminate the duplex structure in an 11 per cent. Si alloy suggesting the limit of the alpha + gamma field to lie between 6 and 11 per cent. Si.

The evidence of the existence of the compound Fe₃Si seems rather weak. The break in the resistivity curve may only indicate the limit of the alpha at room temperature phase and not the presence of a compound. The resistivity determinations of a number of specimens of 14.3 per cent. Si, all in the fully annealed condition and

¹⁸ G. Phragmén: Constitution of the Iron-silicon Alloys. *Jnl. Iron and Steel Inst.* (1926) **114**, 397.

quenched from different temperatures, would throw light on this important point. If the break merely indicates the limit of solubility of the compound in the alpha phase, then, from analogy with other systems, it is very probable that this phase line will not be vertical but will follow the contour suggested by Phragmén; *i. e.*, the solubility will change with temperature.

The writer has difficulty in appreciating why Mr. Corson assumes that the phase lines *HI* and *FI* will meet at the location of the compound Fe_3Si . The line *HI* merely indicates the change of concentration of Si in the alpha phase, and the line *FI* the change of concentration in the delta phase, with changing temperature. Thus, silicon being more soluble in the alpha phase (or the delta phase, Phragmén having shown these to be the same thing) than in the gamma phase, the delta-gamma transformation is lowered and the gamma-alpha change raised. This follows directly from the equation $-\Delta T = RT^2 \frac{(x_1 - x_2)}{L}$ where x_1 is the solubility of the solute in the high-temperature phase and x_2 the solubility of the solute in the low-temperature phase, the other letters having the usual meanings applied to them in physical chemistry. There is no special reason why these phase lines should intersect at the line indicating the location of the compound Fe_3Si (or the change in solubility of the compound in the alpha phase). In the systems Fe-Mo and Fe-W, for example, no such intersection occurs although it does so in the case of the Fe-C system. However, in this last system, the carbon being more soluble in the gamma phase than in the alpha (or delta) phase, we find the delta-gamma transformation raised and the gamma-alpha change lowered.

It is most interesting to observe that Fe-Si alloys can be rendered ductile and machinable by suitable heat treatment. This knowledge should result in the increased use of these acid-resisting alloys whose most troublesome feature in the past has been their liability to fracture. The observation that the resistance to corrosion increases the nearer the silicon content approaches to 14.5 per cent. is significant. This would suggest that in these high-silicon alloys only one phase was present. Were the corrosion tests carried out on annealed samples or cast specimens?

The fact that the limit of solubility of carbon in Fe-Si alloys occurs at 0.7 per cent. C is of interest, and that any carbon above this is eliminated as graphite. Some years ago the writer attempted to make some high-silicon acid-resisting alloys. Many failed on account of cracks, and on examination showed graphite. This would appear to indicate that the Fe_3C had decomposed after solidification resulting in cracking.

M. G. CORSON (written discussion).—When I say "the alpha + delta range" I do not indicate a duplex phase range, but a range of chemical and mechanical inhomogeneity, which is conducive to brittleness and excessive corrosion. Alpha iron is always considered as being identical with delta iron.

Also, the "markings" do not represent a second constituent. They have no definite boundaries. They result only from a lack of homogeneity—a duplex structure at a higher temperature range—and are the more noticeable with stronger lack of homogeneity. For instance, an alloy with 4 per cent. Si was a nearly pure gamma; it showed no markings but tarnished quickly. Another alloy with 13 per cent. Si was nearly pure delta—or Fe_3Si . That also showed no markings, but had yellow streaks. An alloy with 9 to 10 per cent. Si consisted of (roughly) 50 per cent. gamma and 50 per cent. delta, therefore it showed the maximum of markings, particularly on quenching.

Replying to Mr. Hay: The "barley-shell" markings in a number of the photomicrographs do not indicate the existence of a duplex structure at low temperatures but only at a transition period at high temperatures. As long as this duplex struc-

ture is not too pronounced at the corresponding high temperature, the markings may not appear; therefore neither an alloy with 4 per cent. silicon nor an alloy nearing the Fe_3Si compound (say 13 per cent. Si) can be expected to show such markings. I certainly had no definite reason for extending the duplex range exactly up to 14.3 per cent. silicon; this was done only hypothetically, as was stated in the paper. I had no means at my disposal for the delicate work of ascertaining the actual ranges of various fields in the diagram proposed.

I consider the evidence for the existence of the Fe_3Si rather strong. Alloys that represent only a limited range of solid solutions show a continuous increase in electric resistivity, a maximum (sharp or shallow) occurring at the limit of the alpha saturation. As long as a maximum of electric resistivity occurs somewhere within the alpha range, these solid solutions must be considered as formed by two chemical "individuals" located at the minimum points—in this case, iron and the Fe_3Si compound.

More recently, I have found that in another system—the Fe-Al series—almost identical conditions take place. The alpha (or delta) solid-solution range stops sharply at the concentration of the FeAl compound, which again forms the second minimum of the resistivity curve, indicating that a continuous change from Fe to FeAl takes place without change in the lattice type.

Quenching high-silicon alloys for resistivity determinations serves no purpose. No matter what quenching medium is used, the samples become embrittled to such an extent that no two identical figures can be obtained. This also is stated in the paper.

Murakami's alpha range boundary line must be definitely rejected. An alloy containing less than 14.3 per cent. silicon does not become duplex on quenching from high temperatures, while alloys containing between 14.3 per cent. and 18 per cent. silicon refuse to become homogenized in this way and do not even show traces of a previous dissolution (new grain-boundary formation) followed by a reprecipitation when slowly cooled after a long sojourn at high temperatures (1100°).

The continuous decrease in the lattice parameters until a second phase appears at exactly 14.3 per cent. silicon was established by both Bain and Phragmén. It cannot be explained just as a matter of incident. When the solid solubility stops and changes to a duplex structure so sharply at a concentration exactly corresponding to a definite compound (in this case quite to be expected on account of the analogy between carbon and silicon), there must be a definite reason for it. In years past, when other authors have insisted that the alpha range in the iron-silicon alloys ends strictly at the Fe_3Si composition, this assumption has never been criticized as being "rather weak," although no evidence of a micrographic or a physical nature has been introduced.

I repeat that my whole diagram is highly hypothetical, offered only as a picture that might smoothly explain the peculiarities of iron-silicon alloys. I believe it serves this purpose by explaining the brittleness and the corrosion resistance. It is hopeless to search for the absolute truth in systems so difficult of investigation as that of FeSi alloys until large and well-equipped laboratories shall be run by the state for this specific purpose.

Mr. Armstrong does not criticize any of my conclusions or observations, but gives a rather indefinite picture of the processes which, according to his ideas, might take place in alloys of this kind. The fractures in the high-silicon alloys of the alpha range always run through the grains, and never along their boundaries, which shows that the brittleness is inherent to the grain while the boundary cement is sufficiently strong. The whole theory or hypothesis that I have formulated has for its purpose the explanation of this intracrystalline brittleness.

Critical Points in Chromium-iron Alloys

By A. B. KINZEL,* NEW YORK, N. Y.

(New York Meeting, February, 1928)

SINCE the exposition of the behavior of certain iron alloys by Sykes¹ involving the existence of an austenite loop and the discovery of such a loop in the chrome-iron system by Bain,² there has been much conjecture both on his part and on the part of metallurgists in general as to the exact shape and location of this loop. In previous work commercial steel has been used and the microscope has been employed to locate the critical points so that the position of the loop has been quite approximate. Numerous attempts have been made to measure the critical points of the carbon-free alloys but all of these for one reason or another have failed. A satisfactory method for studying these phenomena is presented here.

MATERIAL

The first difficulty in this study was to obtain pure chromium-iron alloys. This has been overcome by melting in a vacuum electrolytic iron and chromium analyzing 99.84 Cr, Fe and C. A pure magnesite crucible was used and the melt allowed to solidify in the crucible. A typical analysis is chromium, 10.10 per cent., carbon, 0.006 per cent., silicon and manganese nil. To overcome the problem presented by segregation, ingots were made into wire 0.04 in. in diameter. This was accomplished by hand-forging the ingots into rods, using an oxyhydrogen flame for heating, in order to avoid carbon. Subsequently the rods were swaged to wire, the heating being carried out in hydrogen. Thus local segregation was eliminated although differences in analysis between portions 50 ft. apart were noted.

An electric-resistance method was first tried to determine the critical points, but due to the physical defects in the wire this failed. Bain had previously shown the presence or absence of critical points in a qualitative way by observing the sag in a catenary. The author has devised the following method which gives an accurate determination of the critical points from expansion-temperature curves of suspended wire, a special telescopic dilatometer being used for the purpose.

* Union Carbide and Carbon Research Laboratories, Inc.

¹ W. P. Sykes: The Iron Tungsten System. *Trans.* (1926) **73**, 968.

² E. C. Bain: Nature of the Alloys of Iron and Chromium. *Trans. Amer. Soc. Steel Treat.* (1926) **9**, 9.

APPARATUS

The wire is suspended in a special vacuum furnace together with a platinum, platinum-rhodium thermocouple calibrated in the usual

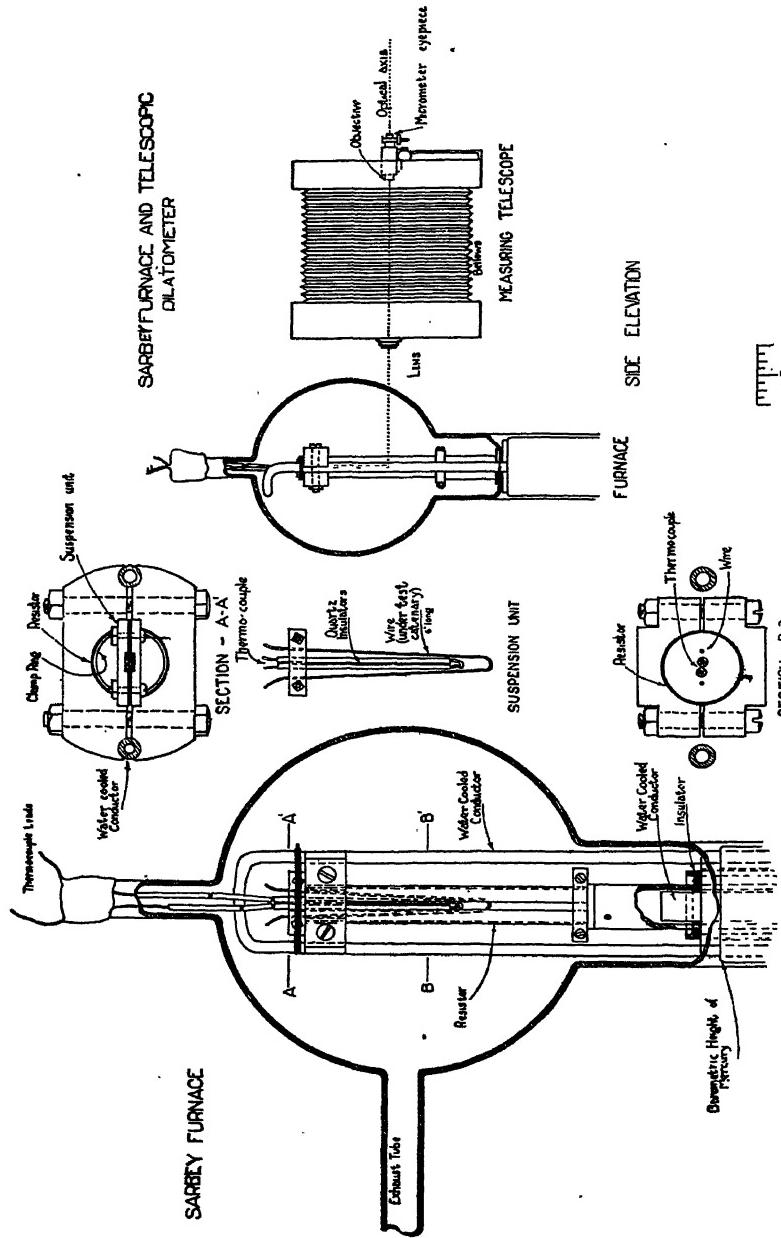


FIG. 1.—APPARATUS FOR DETERMINING CRITICAL POINTS OF WIRES.

manner. This furnace was designed by Sarbey.³ It consists essentially of electric resistors operating in vacua over a barometric height of mercury. The leads are brought up through the column of mercury and are water-cooled. The wire and couple are heated in a vacuum by means of the resistor elements of the Sarbey furnace. These elements are so placed that slits between them are parallel to the plane of the suspended wire, making the end of the wire loop visible through the glass bulb of the furnace. The entire arrangement is shown in Fig. 1. On heating the furnace, sufficient light is produced so that by means of an ordinary camera lens the image of the wire may be projected on a ground-glass screen. The screen, after serving to locate and center the image, is removed and the image is then viewed through a microscope magnifying 100 diameters. The eyepiece of this microscope is fitted with a micrometer scale of the usual type, with movable cross-hair, one division representing 0.000716 ± 0.000007 mm.

Great care was taken to have the whole apparatus very rigid so that there was no motion of the microscope with respect to the suspension unit. The image was set with the lower end of the wire loop near the top of the field and the motion of the end of the loop was followed with the cross-hair of the microscope. Temperature readings were taken simultaneously with position readings. The method of suspending the wire precludes any absolute expansion values being obtained but does not affect relative values. The wire was held in a clamp laid across the top of the resistor tube and fastened to a water-cooled frame in the furnace. The ends of the wire in the clamp never reach more than 600° C. even though the part in the furnace is at a temperature of 1400° C. However, it is estimated from the results of readings taken with the thermocouple in various positions that the temperature of the wire 1 in. from the clamps is invariably within 10° of the working temperature. This means that 5 in. of the wire undergoes transformation changes at the same instant. The changes that take place in the remaining inch are continuous, so that they result merely in changing the apparent rate of expansion and give no jogs in the curve.

It is estimated, from a consideration of the methods used, that the temperature of transformation has been measured accurately to within 10°. Five check runs on one specimen gave results varying by less than 7°. However, on account of the above mentioned conditions, no claim for accuracy is made for the absolute rate of expansion, although the relative rates of the alpha and gamma phases may be considered fairly accurate.

³ The Sarbey furnace was developed by Mr. Sarbey of the Union Carbide and Carbon Corporation, Kemet Laboratories, and since its development has found considerable application in these Laboratories. This is the first public description, to the best of the author's knowledge. It should be noted that patents on this furnace are pending.

METHOD

In order to insure freedom from difficulty caused by small kinks in the wire, it was first heated to a temperature above the maximum expected,

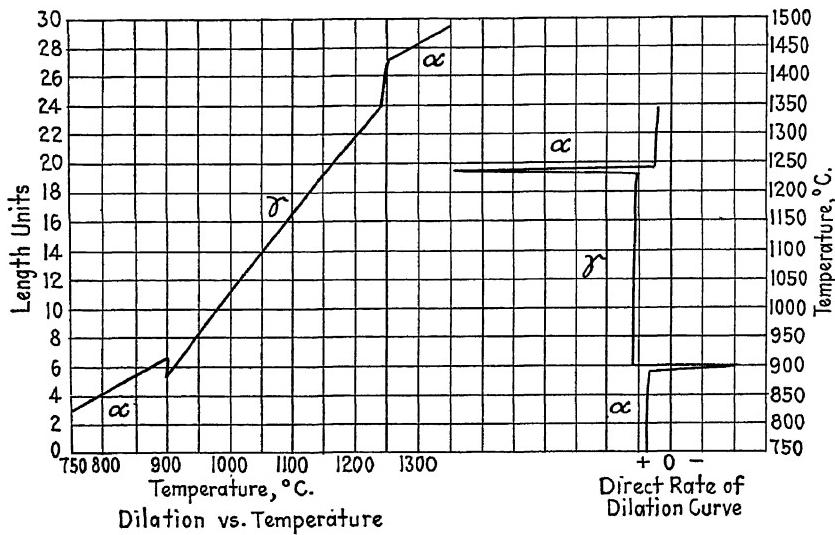


FIG. 2.—CURVES OBTAINED WITH THE TELESCOPIC DILATOMETER, SHOWING CRITICAL POINTS OF 10.1 PER CENT. CHROMIUM-IRON ALLOY.

held for a time and slowly cooled. The subsequent reheating to the first critical point was slow and was repeated to just below this point before

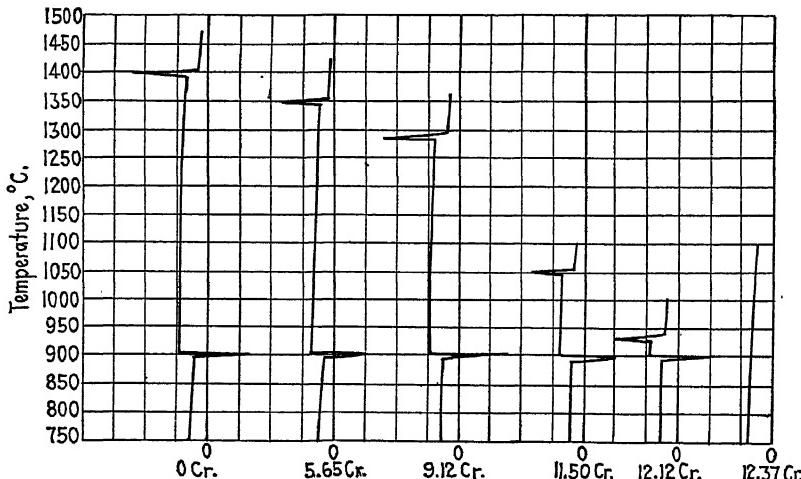


FIG. 3.—DIRECT RATE DILATION CURVES FOR CHROMIUM-IRON ALLOYS.

final readings were taken. One of the striking things about these curves is the lack of hysteresis. This may be accounted for by the very low

carbon. It is probable that extreme sluggishness exists only with the carbon-chromium combination. The preliminary heatings also help to eliminate hysteresis. The method employed in taking the curves follows: After determining the approximate location of the critical point,

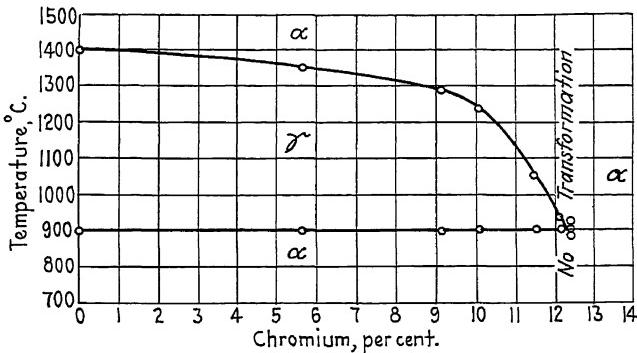


FIG. 4.—TRANSFORMATION POINTS IN PURE CHROMIUM-IRON ALLOYS.

a number of readings were taken at this point at short intervals, with long time temperature conditions. The accompanying curves are typical of the direct "temperature-dilation" heating curves and "rate of dilation-temperature" curves obtained. It will be seen that the lowest point of the wire loop drops as the temperature increases until the lower critical point is reached. At this point, due to contraction, the loop moves up. With further temperature increase the loop elongates at a different rate until the upper critical point is reached, when the loop drops suddenly. Further temperature increase is accompanied by another change of slope. The new slope approximates the original one.

There was some difficulty in locating the end of the loop in the microscopic field and in maintaining the sharpness of the image, but with some experience, accurate dilatometric curves were obtained. On account of the chemical segregation, it was considered necessary to analyze each wire sample after determining the critical points.

RESULTS

The chemical analyses and the corresponding critical points are shown in the temperature-chromium content equilibrium diagram (Fig. 4) and in Table 1. A general check on the apparatus and method was

TABLE 1.—*Chemical Analysis and Critical Points*

Cr, PER CENT	A_4 , °C	A_3 , °C
0	1400	900
5.62	1350	900
9.12	1290	900
10.10	1240	900
11.50	1050	900
12.12	935	900
12.37	None	None

obtained by the determination of the critical points of electrolytic iron giving the well known points at 900° C. and 1400° C.

The lower critical point is found to be unaffected by chromium in spite of previous belief that it occurred at higher temperatures with higher chromium contents.^{2,4} Analysis of the carbon content of the wire that was used showed less than 0.01 per cent. The upper curve shows a gradual decrease of the A_4 point, which decreases rapidly at about 9.5 per cent. chromium. There is some question in the author's mind as to the shape of the loop at the merging of the A_3 and A_4 points, but there are no facts to show that this is other than a sharp angle. The end of the austenite loop is located at 12.2 per cent. This is much lower than had been previously supposed.

An attempt has been made to find the law followed by the upper curve of the loop. This curve may be readily expressed mathematically as an oblique hyperbola. However, this has no physical meaning to the author; moreover, he has been unable to tie up even the simple relations of the asymptotes with any physical conception.

The application of the phase rule to the loop has been considered. According to the phase rule there should exist between the alpha and the gamma phases both at the upper and lower boundaries of the loop, a two-phase region. However, microscopic study of the alloys has shown no indication of any such region and this dilatometric study further fails to reveal it. Hysteresis may have obscured the region. This might mean that the true initial transformation takes place below 900° C., proceeds very slowly for a short temperature interval and then increases quite rapidly, giving the effect of an isothermal change at 900° C. A similar condition could exist with regard to the upper curve. Possibly the curves as drawn are branches of two different loops, the inner and the outer, although this is not probable. Still another possibility is that the border zone is so narrow as to be practically negligible.

Recently an equilibrium diagram of the chromium-iron system due to Oberhoffer and Esser⁵ has appeared unaccompanied by any descriptive matter. The A_4 line agrees in character with that here presented but slopes somewhat more steeply. The end of the loop coincides with that here shown. The A_3 line, however, runs from 900° C. with zero chromium to 900° C. at the end of the loop, not as a straight line as here shown but as a curve dipping to 850° C. at some 8 per cent. chromium. From purely theoretical considerations, the author believed that such a dip might occur and although it was searched for in the present study, no points lower than 900° C. were evidenced.

⁴ M. A. Grossman: Nature of the Chromium-iron-carbon Diagram. *Trans. (1927) 75, 214.*

⁵ P. Oberhoffer: Entwicklung der Qualitätsfrage. *Stahl und Eisen (1927) 37, 1512.*

CONCLUSIONS

1. The chromium-iron loop runs from 0 to 12.2 per cent. chromium.
2. Its upper boundary runs from 1400° C. to 900° C. following an oblique hyperbola and its lower boundary runs from 900° C. at 0 chromium to 900° C. at 12.2 per cent. chromium.
3. The telescopic dilatometer here shown (Fig. 1) used in connection with the Sarbey furnace, is an excellent apparatus for determining critical points in wire, which is a most convenient form for this type of work.

ACKNOWLEDGMENTS

The author wishes to express his appreciation of the coöperation of his colleagues in the Union Carbide and Carbon Research Laboratories, particularly of the work done by C. E. Plummer in preparing the ingots; of the general assistance of J. J. Egan, W. Bohnet and H. Willis in carrying out the tests, and of the helpful discussions with E. C. Bain, M. G. Corson and T. W. B. Welsh. He also wishes to thank Dr. R. D. Hall of the Westinghouse Lamp Co. for his coöperation in swaging the rods.

DISCUSSION

P. A. E. ARMSTRONG, New York, N. Y.—The diagram is very interesting, particularly the continuation of the alpha phase. I understand that a brittling constituent might have something to do with delta iron. As there is no delta iron, but there is brittleness, I am wondering what has happened.

E. C. BAIN, Long Island City, N. Y. (written discussion).—I have no intention of discussing at length this valuable work of my colleague, but I desire to take this opportunity to express my indebtedness to Dr. R. D. Hall of the Westinghouse Lamp Co. for generously consenting, at my request, to make the wires which were later used in these experiments. He was at some pains to arrange to swage the iron-chromium bars by special means, which required considerable time.

Furthermore, I should like to read into the discussion a private communication which I have from Dr. Esser, of Aachen, Germany, whose iron-chromium diagram has already been referred to. The translation would be about as follows:

"1. *Preparation of the Alloys.*—The iron-chromium alloys were prepared in vacuum in the molybdenum furnace from the purest electrolytic iron (0.01 per cent. C, trace Si, Mn, P, S) and a chromium-rich addition alloy containing 0.02 per cent. C. The final alloys contained 0.01 per cent. C. The nitrogen content does not come into question since they were melted in vacuum.

"2. *Determination of A_1 and A_4 .*—The critical points were investigated in vacuum, partly by thermal means according to the differential method of Roberts-Austen, and partly by our own dilatometer with close adjustment for expansion measurement.

"3. *X-ray Determinations.*—As for the X-ray investigation, the alpha-iron and gamma-iron lines show simultaneously on the film at the temperature of the transformation, in accord with what would be accepted on the basis of physical chemistry for the zone of transformation between ferrite and austenite, and the two phases—alpha and gamma iron—exist side by side. This conclusion also is born out by the thermal investigation in that the transformation in no case takes place at a constant temperature. In other words, there was found no thermal halt-point other than a transformation interval. This two-phase region must always be found in all alloy systems which exhibit a restricted gamma iron or austenite zone."

It might perhaps be mentioned that the first occasion upon which I observed the critical point in iron by any such means as described here was in the case of a ribbon filament of iron in a tubular "lamp." The Research Department of the National Lamp Works had supplied Dr. Jeffries and me with small exhausted tubes of glass having low atomic weight, in which a flat ribbon of iron was clamped as a filament. They were used in the X-ray study of iron at elevated temperatures. When current was passed to heat the filament, the sudden shrinking of the ribbon was very noticeable at the Ac_3 point. A fairly flat catenary shows the effect most clearly, since the vertical motion of the center of the wire or ribbon exaggerates the actual length-change.

Where the wire or ribbon is heated by the current passing through it, a loop or catenary is necessary, but when externally heated, as in Mr. Kinzel's experiments, a straight length of heavy wire replacing the long loop would probably serve as well or perhaps better.

The measurement of the properties of metals in vacuum at elevated temperatures by such ingenious devices as described here should be of general interest to many metallurgists who will see valuable extensions possible by this principle.

There is one circumstance which introduces some question as to the accuracy of the measurements described here. Unfortunately, the actual measurements of temperature and length are not given, and one must base conclusions on the charts of Fig. 3. In these charts, the coefficient of expansion is shown as decreasing with increase in temperature, whereas, according to innumerable measurements on pure iron (and many steels), the reverse is true. It is impossible to determine whether or not this disagreement lies in the experimentation or in computation or in drawing the charts.⁶

There is a very good reason why this point should be well established. If the coefficient of expansion increases with temperature, as has previously been believed, the length-temperature curve for the alloys is such as to corroborate the view that the state of affairs above the austenite loop is merely an extension of the conditions below the austenite temperature. (This is most pronounced in the consideration of alloys just within and just without the chromium limit for austenite formation.) The magnetic susceptibility curve of pure iron, for example, is such as to indicate that the changes with temperature are only *interrupted* by the gamma phase, and a logical extrapolation of the curve below 900° C. fits perfectly the portion above 1400° C. In all probability, the length change is the same, whereas in Fig. 2, Dilation vs. Temperature, a logical extension of the lower alpha line would not fit the upper alpha line. It is not sufficient that the slope be similar—the actual extension should be a real extrapolation. Indeed, Westgren's X-ray work indicates that his delta (upper alpha) crystals were expanded in accord with the equation fitting the lower alpha thermal expansion.⁸ If the change in coefficient of expansion were in the opposite direction, as according to Kinzel, an anomaly would result, in that a change in the nature of a phase would have to occur abruptly with a slight change in composition or temperature, for certainly the expansion curve for a 13 per cent. Cr alloy is smooth and unbroken.

⁶ See, for example, P. Hidnert and W. T. Sweeney: Thermal Expansion of Alloys of the "Stainless Iron" Type. U. S. Bur. Stds. Sci. Paper No. 570.

P. Weiss and G. Foëx: Etude de l'aimantation des corps ferromagnétiques au dessus du point de Curie. *Archiv. sc. et nat.* (1911) **31**, 89; *Jnl. Phys.* [5] (1911) **1**, 745. A better diagram, based on the same work, is that of M. C. Neuberger: Röntgenographie des Eisens und seiner Legierungen, 41.

⁸ A. Westgren: Roentgen Spectrographic Investigations of Iron and Steel. *Jnl. Iron and Steel Inst.* (1921) **103**, 303.

A. Westgren and G. Phragmén: X-ray Studies of the Crystal Structure of Steel. *Idem* (1922) **105**, 241.

It may reasonably be assumed that the error is not in the conception of the interrupted alpha phase but in the measurements or computations of the investigator, since Kinzel shows even the familiar pure iron with the reversed change in coefficient.

We shall probably find upon further investigation with still more refined apparatus that the austenite region and the ferrite region of the diagram are separated by a two-phase zone of narrow dimension as found and discussed by Esser, but on the whole it would seem likely that the general contours of the austenite region have been far more accurately located by Kinzel.

H. STRY, Philadelphia, Pa.—I would like to call attention to the expansion diagram in the paper. We have an alpha region and a gamma region and delta (or alpha) region. We know from electric and magnetic properties that there is some continuity between this alpha region and this delta region. Now I wonder how these two should be connected in Fig. 2 left. For instance, in 10 per cent. chromium, would there be an inversion or a break in the curve, or is the expansion incorrectly measured? There was a good opportunity here to find that out, but apparently it has been missed.

R. HAY, Glasgow, Scotland (written discussion).—The diagram derived by Mr. Kinzel for the gamma-alpha transformations in Fe-Cr alloys presents some novel and very suggestive features. The persistence of the alpha-gamma change at a constant temperature of 900° C. is remarkable. This, together with the fact that he found no hysteresis, suggests that chromium is equally soluble in the alpha and gamma phases at this temperature. It is also worthy of note that the alpha-gamma change at the high temperature (1400° C.) shows only a very slight depression up to about 9 per cent. Cr, pointing to the same equal solubility at this high temperature. When the chromium exceeds a certain amount—about 12 per cent.—it may stabilize the alpha iron lattice but if the amount of chromium falls short of this required figure, then at 1400° C. the alpha iron transforms to the gamma configuration, which in turn again reverts at 900° C. to the alpha state. If such were the mechanism of the changes, the diagram in its ideal form would be a simple rectangle.

In a later paper⁹ than the one referred to in this paper—and no doubt published after this paper was written—the late Professor Oberhoffer gave further data relating to this system. He found a marked hysteresis of both the A_4 and the A_3 points and also that the A_4 change was sharply depressed by even small amounts of chromium. This would indicate that chromium is much more soluble in the alpha phase than in the gamma phase, and consequently a rise in the A_3 transformation would be expected. However, Oberhoffer, like Mr. Kinzel, found that the A_3 point did not rise; in fact, he found that it actually fell slightly although at 9.9 per cent. Cr the A_{C_3} occurred at 900° C. This line of argument would suggest that Mr. Kinzel's diagram is the more correct. Probably the author (Mr. Kinzel) will supply us with further physical data of the same high order of accuracy to substantiate even more fully this new diagram which he has presented to us.

A. B. KINZEL (written discussion).—Mr. Armstrong assumes that brittleness in certain chromium-iron-carbon alloys may be due to delta iron and, there being no delta iron shown in the diagram beyond some 12.3 per cent. chromium, there should be no brittleness. Passing over the question as to whether or not brittleness is due to delta iron and assuming that it might be, the theory is not at all inconsistent with the data here presented. In commercial alloys a certain amount of carbon is present. This carbon causes the austenite loop to be carried out much further than 12.3 per

⁹ P. Oberhoffer: Zur Kenntnis des Zustandsdiagramms Eisen-Chrom. *Stahl und Eisen* (1927) 47, 2021.

cent. chromium, particularly at microscopic regions of high carbon concentration in the alloy. Thus, in commercial material there would be local areas which would undergo the alpha-gamma-delta transformation even when the chromium content is considerably in excess of 12.3 per cent.

The communication from Dr. Esser presented by Dr. Bain is in brief a restatement of his experimental conditions and results. Dr. Esser has undoubtedly done a fine piece of work and his location of the alpha and gamma phases coexistent is in line with what the writer expected to find. This whole matter has already been treated in the paper proper so there is no need to discuss it further, except to state that probably differences in the material used rather than methods of measurement are the cause of any lack of agreement which exists. Dr. Esser used chromium prepared by the Thermit method with attendant nitrogen.

Mr. Bain's suggestion that a straight length of heavy wire could have been used instead of the long loop suspended in the Sarbey furnace is interesting, as this was the arrangement first tried. It was found that with moderate thicknesses of wire the twisting action due to temperature gradients set up on initial heating were sufficient to make the end of the wire touch the molybdenum-resistor sheets and cause short circuit and fusion. Accordingly a loop was used.

Mr. Bain says that the rate of change of coefficient of expansion or second derivative of the dilation temperature curve should be opposite in sign to that shown in the curves and the author would add that the absolute value is also much less. This brings up an interesting point in connection with this type of work in general; that is, that the figures should not be used without careful consideration of the experimental methods by which they were obtained. The author has taken great pains to state definitely, on page 303, that the method of suspending the wire precludes absolute expansion values. It is further stated that one end of the wire is kept fairly cold and there is a region of about 1 in. in which there is a temperature gradient from the cold end to the maximum temperature in the wire. As the temperature of the wire proper increases, the gradient in this zone becomes steeper and steeper, so that there is a continuously decelerated lengthening effect due to this zone on heating up and vice versa on cooling, giving the same effect as if the change in coefficient of expansion of the material were opposite in sign. This is particularly emphasized when part of the zone in question undergoes the gamma contraction. Thus, there is a very simple experimental explanation for the shape of the curves and it is definitely shown that the apparent anomaly is not due to errors in measurements or computations.

Dr. Styri brings up a very interesting point. The 13 per cent. chromium curve indicates that there is no inversion. It is well recognized that the coefficient of expansion of gamma iron is greater than that of alpha iron and the measurements here given bear out this statement. Accordingly, the only way in which direct continuity from alpha to delta could exist would be either to have an extremely large contraction at the alpha-gamma point with a relatively small expansion at the gamma-delta point or actually have two contractions. It is very difficult to conceive of either of these things and we must conclude therefore that there is no direct length continuity from alpha to delta when the gamma transformation takes place. It seems to me that this is a matter for speculation rather than experimentation, although it is possible that with absolute measurements the relation between original alpha size and final delta size could be more accurately determined. This was beyond the scope of the research in which we were interested.

The author wishes to thank Prof. R. Hay of Glasgow, Scotland, for the criticism presented and is thoroughly in accord with his line of reasoning. As stated in the paper, the writer is much interested in the remarkable constancy of the 900° alpha-gamma change and the lack of hysteresis in this zone, and hopes to find out more about the nature of this phenomenon.

The Neumann Bands in Ferrite*

BY C. H. MATHEWSON† AND G. H. EDMUNDSD,‡ NEW HAVEN, CONN

(Philadelphia Meeting, October, 1928)

ABOUT fifty pages of Henry M. Howe's profound treatise, "The Metallography of Steel and Cast Iron," are devoted to twinning with special reference to the origin, nature and general significance of the Neumann bands in ferrite. Howe believed with Osmond and Cartaud¹ that the Neumanns are mechanical twins and his careful observations leave no doubt that these straight-sided narrow bands habitually occur parallel to trapezohedral planes of form {211}.

Attempts to develop the structure of the bands by various methods so that their identity could be established beyond question have not been conspicuously successful. Howe thought that they deflected slip bands. Some of the etching figures which have been developed within and adjacent to Neumann bands support the contention that they are twins. A good example of this effect in ferrite containing 0.6 per cent. of nickel and 1.3 per cent. of phosphorus, originally due to Harnecker and Rassow,² was reproduced in the 1928 lecture before the Institute of Metals Division on twinning in metals.³ In this case, the sides of the figures might represent the traces of cubic planes laid bare by etching a properly oriented grain of ferrite, twinned along a plane of form {211}. Our own observations in this direction may be represented by Fig. 1 which shows in a deeply etched cavity in the boundary region between a Neumann band and the original crystal two small crystal surfaces which resemble the faces meeting at a reentrant angle in the simple cube twinned along a bisecting plane of form {211} as sketched in Fig. 2.

Rosenhain and McMinn⁴ in 1925, after a careful study of slip bands in ferrite containing Neumanns previously produced by shock, concluded

* Originally presented by C. H. Mathewson in the form of a lecture before the combined Washington Sections of the A. I. M. E. and A. S. S. T., May 11, 1928.

† Professor of Metallurgy, Yale University.

‡ Graduate Student, Department of Mining and Metallurgy, Yale University.

¹ F. Osmond and G. Cartaud: The Crystallography of Iron. *Jnl. Iron and Steel Inst.* (1906) **71**, 444.

² K. Harnecker and E. Rassow: Aetzfiguren und Zwillingsbildungen in Eisen. *Ztsch. Metallk.* (1924) **16**, 312.

³ C. H. Mathewson: Twinning in Metals. *Proc. Inst. Met. Div.* (1928) 1.

⁴ W. Rosenhain and J. McMinn: The Plastic Deformation of Iron and the Formation of Neumann Lines. *Proc. Roy. Soc.* (1925) **108**, 231.

that the region of the Neumann band could not be a twin layer since slip bands in traversing it either maintained their original trend or changed direction irregularly in different places, instead of suffering a uniform angular deviation throughout the entire region. This point of view has



FIG. 1.—ETCHING FIGURES AT THE BOUNDARY OF A NEUMANN BAND.

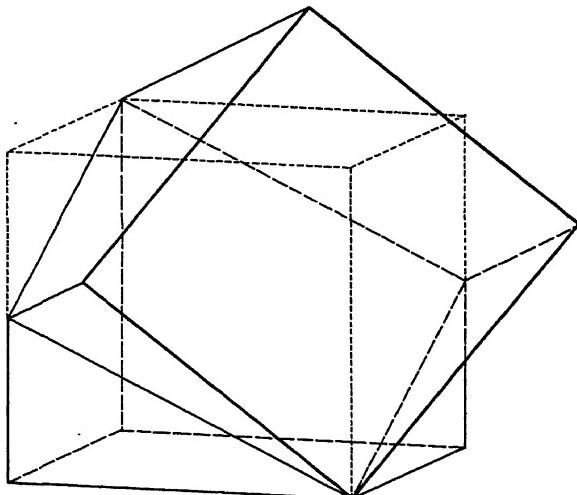


FIG. 2.—SIMPLE CUBE TWINNED ALONG A BISECTING PLANE OF FORM {211}.
— indicates invisible portion of model.
- - - indicates original position of cube above twinning plane.

been emphasized on other occasions; *e. g.*, in discussing Benedicks' suggestion that hardening by cold work may be due to multiple twinning, Rosenhain⁵ asserts that mechanical twinning is unknown in alpha iron.

On account of the present uncertainty concerning the exact nature of slip bands in ferrite, it does not seem possible to predict just how

⁵ W. Rosenhain: The Structure of Metals. *Nature* (1927) **120**, 217.

the process of slip would operate in transferring from the main crystal to a twin band. It is, however, pertinent to emphasize the bearing of some of the particular structural features of the type of twinning under consideration on this question.

The twinning axis [111] is an axis of threefold symmetry and the line of greatest atomic density in the body-centered cubic lattice. Twinning, which may be conveniently imitated by rotating the atoms 60° around this axis, does not change the location of any plane in the surrounding zone, so that slip in the [111] direction along any one or any combination of the three planes of form {211} or of form {110} located in this zone could proceed straight through the twin. We can see no fundamental reason why slip in complicated form, distributed among several of these planes, or slip of the columnar type proposed by Taylor and Elam⁶ could not traverse the body of the twin without any significant deviation from its previous irregular course in the main crystal. The continuation of slip along a given plane into the twin might, however, be resisted by a condition of distortion or change in registry of the atoms on some of the slip planes at the twin boundary.

Other potential slip planes of form {211} or {110} may or may not have a common line of intersection in the twinning plane but in either case the direction of slip must change from crystal to twin much as it might change from one crystal to another.

From these considerations it appears that the conditions observed by Rosenhain and McMinn are not at all incompatible with the view that Neumann bands are mechanical twins.

O'Neill⁷ has recently reviewed much of the evidence bearing on slip and twinning in ferrite. His own experiments were believed to support a theory of "duplex conjugate slip" along cooperating planes of form {211}. Admitting the absence of "perfectly conclusive evidence as to the orientation of the atoms" within Neumann lamellae and considering etch-pit observations misleading or unreliable, the inherent probability of mechanical twinning was favored on the ground of a simple translatory mechanism which would readily yield twinned structures. The latter was clearly foreseen by Osmond and Cartaud⁸ and is chiefly of interest as a demonstration with the modern crystal structure model of *einfache Schiebung* in ferrite, which had been expressed in precise crystallographic form by Mügge⁹ nearly 30 years ago.

⁶ G. I. Taylor and C. F. Elam: The Distortion of Iron Crystals. *Proc. Roy. Soc. (1926)* **112A**, 337.

⁷ H. O'Neill: Deformation Lines in Large and Small Crystals of Ferrite. *Jnl. Iron and Steel Inst. (1926)* **113**, 417.

⁸ *Op. cit.*

⁹ O. Mügge: Ueber Neuere Strukturflächen an den Krystallen der gediegenen Metalle. *Jahr. f. Mineral.* (1899) **2**, 55.

The evidence that Neumann bands are twins was summarized by O'Neill as follows:

- "(1) They have often parallel sides like twins,
- "(2) They deflect slip-bands as twins should do,¹⁰
- "(3) They etch to a different tint from their background, which suggests that they have a different orientation,
- "(4) Parallel ones have identical orientation,
- "(5) The production of a twinned layer by simple deformation of ferrite along (112) planes appears to be easy."

Furthermore, a study of the literature justified certain specific statements to the effect that Neumann bands form

- "(1) Readily in silicon ferrite at room temperatures even by static deformation. (Ordinarily, silicon iron is of very large grain-size and is brittle under shock.)
- "(2) Readily in phosphoric ferrite (1.0 per cent. phosphorus) at 20° C., under conditions of deformation which will not produce them in pure ferrite. (Phosphoric iron is generally of large grain-size and is brittle under shock.)
- "(3) Readily in pure ferrite even by slow deformation at the temperature of liquid air. (At this temperature the ferrite is brittle to shock.)
- "(4) Apparently readily at room temperatures in coarse ferrite produced by high-temperature annealing. Sawing, filing, and polishing, then, appear to be sufficient to produce them. (Coarse ferrite is brittle under shock.)
- "(5) With difficulty in fine aggregates of ferrite. Static deformation, sawing, filing and polishing do not ordinarily produce them, but very rapid deformation does, *e. g.* impact. (Fine ferrite is not ordinarily brittle under shock.)"

SCOPE OF THE PROBLEM IN HAND

The Neumann bands and the familiar curved and forked slip bands are fundamental elements in the chain of structural evidence which must ultimately give a complete picture of the manner in which ferrite crystals yield under various forms of stress. Conflicting opinion concerning the exact nature of both deformational effects makes it expedient to reexamine critically the available evidence and devise an experimental plan which shall be considered competent to clarify these questions.

Present considerations relate exclusively to the Neumann bands and will be presented in the following sequence: First, in order to favor a clear understanding of the problem, the characteristic features of twinning

¹⁰ We have already indicated that each individual case should be examined in this respect on its own merits.

along planes of form {211} in the body-centered cubic lattice will be briefly discussed.

Following this, Mügge's pioneering work will be described in detail, as it appears to have been neglected or misunderstood by all metallurgical writers who have formally discussed this problem and in our opinion comes very close to settling the entire matter.

Finally, the results of an X-ray investigation are introduced to prove that the inner structure of the bands is precisely the structure required by the form of twinning under consideration. It is believed that this should be accepted as a final convincing chapter in the controversy.

CHARACTERISTIC FEATURES OF TWINNING IN THE BODY-CENTERED CUBIC LATTICE

There are many ways of representing the twin relationship as it exists in ferrite, each possessing certain advantages according to the point of view of the writer. McKeehan,¹¹ who first proved the existence of broad twinned areas in specially prepared wires of ferrite, used a stereographic projection in which the relationship of the crystal axes before and after twinning was precisely recorded. To those who are not intimately familiar with the conventional constructions and mathematical methods of crystallography, probably some form of demonstration with crystal models will be most satisfactory.

The four lines joining diagonally opposite corners of the unit cube are of particular importance in the body-centered cubic lattice. Since there is an atom at each corner and one in the center, the distance between atoms along one of these lines is $a_0 \sqrt{\frac{3}{2}}$ and this is the least distance which can occur between atoms in this form of structure. These diagonal lines might therefore be expected to represent strings of closely adherent atoms and the investigations of Taylor and Elam¹² in particular seem to prove that this is the case.

The pinwheel model photographed in Fig. 3 turns around one of these lines which is now seen to be an axis of threefold symmetry. A sufficient number of atoms have been attached to represent the characteristic features of the lattice as seen in this position without the confusing effect of greater numbers. The atom at the center may represent one of the corner atoms or the atom at the center of the unit cube.

If it represents a corner atom, the outer group of six atoms located in the central vertical plane of the model represents corner atoms in adjacent cubes and the two inner groups of three atoms, one in a plane $a_0 \sqrt{\frac{3}{6}}$

¹¹ L. W. McKeehan: Twinning in Ferrite. *Proc. Inst. Met. Div.* (1928) 453.

¹² G. I. Taylor and C. F. Elam: *Op. cit.*

behind and the other in a plane the same distance in front of the central plane, represent center atoms in the same cubes. Each atom is one

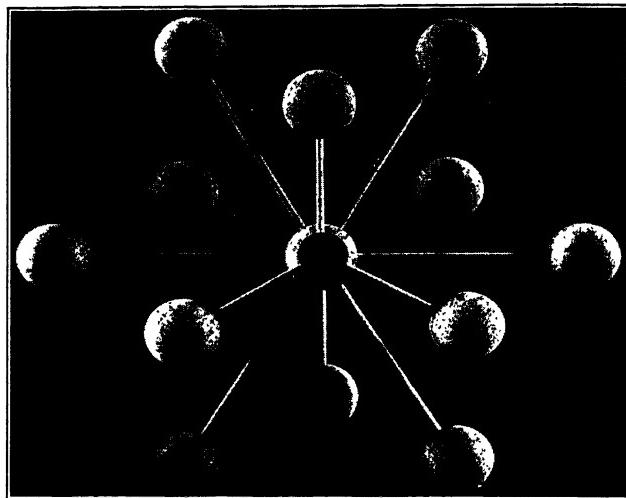


FIG. 3.—PINWHEEL MODEL OF BODY-CENTERED STRUCTURE CONSTRUCTED AROUND AN AXIS OF THREEFOLD SYMMETRY, [111].

member of a close-packed string normal to the plane of the paper. It is thus seen that the strings of atoms fall into three groups, each group

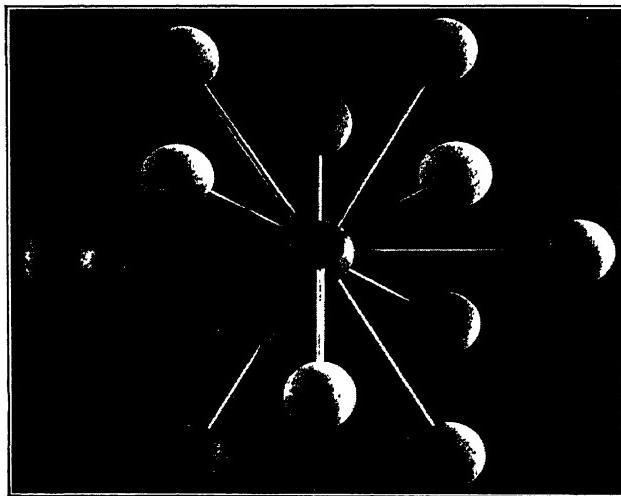


FIG. 4.—PINWHEEL MODEL OF FIG. 3 ROTATED INTO TWIN POSITION.

having atoms at one level arranged in isosceles triangles. Twinning transposes the level of atoms in two of the groups as shown in the accompanying Fig. 4.

There are two simple forms of rotation which will result in twinning, *i. e.*, change the structure shown in Fig. 3 to that shown in Fig. 4. First a clockwise or counter-clockwise rotation of 60° , 180° or 300° around the central axis, and second a rotation of 180° around any one of the three axes parallel to the short sticks in the model, which are coplanar and perpendicular to the three related twinning planes of the crystallographic form $\{211\}$. This in the case of the vertical axis is, of course, equivalent to turning the model around as one would turn the pages of a book.

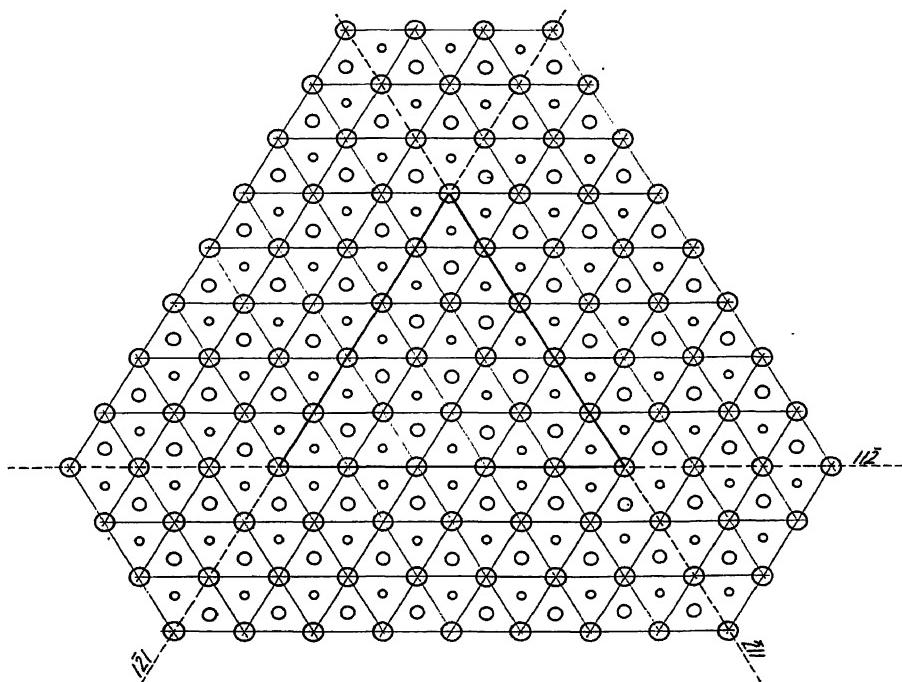


FIG. 5.—TWINNING ALONG THREE RELATED PLANES OF FORM $\{211\}$ IN THE BODY-CENTERED CUBIC LATTICE. PLANE OF PROJECTION = (111).

Atoms in the plane of the projection and fourth, seventh, etc., planes above shown by large circles; in the second, fifth, eighth, etc., planes by small circles; and in the third, sixth, ninth, etc., planes by circles of intermediate size.

Obviously the term twinning implies that two parts of the same crystal or model stand in a twin relationship and this effect is secured by confining the rotation to any appropriate part of the model. Thus a 180° rotation of the upper half around the vertical axis twins this part with respect to the other half.

This is an atomic picture of the twinning which is usually represented by cutting a cube in halves along the twinning plane and fitting the parts together in the reversed position, as shown in Fig. 2, except that in the

present model no attention was paid to the location of cubic boundary planes.

Referring again to Figs. 3 and 4, it is quite evident that as an alternative to the rotational methods of changing one structure into the other, the strings of atoms corresponding to the balls at the extremities of the short sticks may be moved backward or forward to bring about the desired adjustment. There is no doubt that the atomic movements which actually occur when a twin crystal is formed are movements of translation rather than of rotation with certain characteristic restrictions depending on the form of twinning. Thus, in the present case it is not

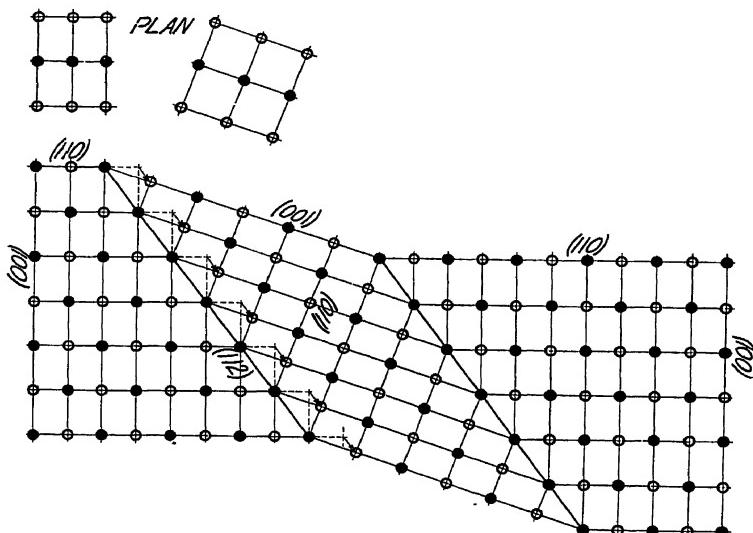


FIG. 6.—TWINNING ALONG THE PLANE (112) IN THE BODY-CENTERED CUBIC LATTICE.
PLANE OF PROJECTION = (110).

possible to move the strings of atoms up and down independently; they must move together in a plane or at least in coherent groups of some sort. The fact that Neumann bands commonly occur as lamellae parallel to planes of form {211} indicates that the strings move coherently in these planes.

A careful consideration of Fig. 5, which is a simple vertical projection on the plane (111) of the atoms in a triangular prismatic block possessing the structure of Fig. 3, completely surrounded by atoms possessing the structure of Fig. 4, will make it apparent that the outer, or twin structure, may be obtained by sliding the {211} planes of the original crystal on one another parallel to any side of the triangle in downward steps amounting to one-third of the vertical distance between exactly similar planes.

A horizontal projection in a plane normal to one of the twinning planes, shown in Fig. 6, is of assistance in visualizing these movements.

Some of the quantitative features of this transformation are as follows: The dodecahedral plane (110) shown as a surface plane changes to a cubic surface plane (001). The distance between the top and bottom surface planes is reduced 29.28 per cent. by twinning under these conditions. The distance between atoms on the twinning plane in the direction of translation is $a, \frac{\sqrt{3}}{2}$ in Ångströms and the movement from plane to plane is one-third of this distance. The least distance between atoms across the twinning plane is 9.2 per cent. less than the least distance between atoms in the unchanged lattice.

The other possible twinning planes of form {211}, nine in number, are distributed around the three remaining threefold axes of symmetry in groups of three, each similar in all respects to the group which has just been discussed in detail. In order to represent this complex situation graphically it is advantageous to designate the relative positions or orientations of the various planes by points at which they become tangent to the upper surface of a sphere and then project these points into the equatorial plane along lines which are directed to the south pole. This is the stereographic projection commonly used in crystallography. A good description of it with directions for performing many of the constructions may be found in Dana's Text-book of Mineralogy.¹³

A projection including most of the important planes of the isometric system is given in Fig. 7. The central point represents the plane (001) at the upper extremity of the vertical crystallographic axis. The straight lines radiating from the center are projected arcs of great circles, or meridians, joining the north and south poles of the sphere of reference. The characteristic zone relationships of the 12 twinning planes are exhibited by the four projected upper halves of great circles which intersect to form a four-pointed star.

Each of these 180° arcs passes through the projected poles of three twinning planes indicated in the figure by heavy black circles and constitutes a zone whose axis is a line joining the center of the sphere with the pole of a plane of form {111} 90° removed from all points on this arc. These poles are shown as black squares.

The positions of all planes in a twin may be found by turning the sphere 60° around one of these zone axes of form [111] or 180° around an axis joining the center with the pole of a twinning plane lying in this zone and projecting the reoriented poles of all planes into the original equatorial plane. Thus, the projection shown in Fig. 8 was obtained by rotating the sphere 180° around the polar axis of the twinning plane (211). The indices of all planes are referred to axes which move with the plane and therefore do not change during the rotation. Twinning around

¹³ 3d Ed. New York, 1921. John Wiley & Sons.

the axis of another twinning plane in the same zone (of axis $[\bar{1}11]$) would produce the same structure but change the indices of corresponding planes.

In Fig. 8, the south pole of the sphere has rotated to the position shown at $(00\bar{1})$ in the projection and the great circles passing through this point correspond to original north and south meridians. The great circle crossing these meridians represents the primitive circle of Fig. 7.

The projection shown in Fig. 9 represents the structure of a twin corresponding to another one of the zones represented in Fig. 7. It was obtained by rotating the sphere 180° around the polar axis of the plane $(\bar{2}11)$.

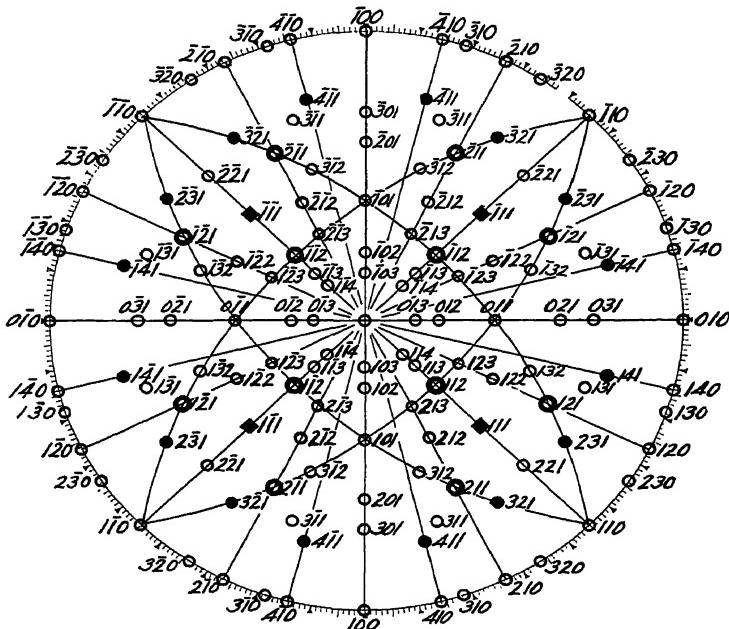


FIG. 7.—STEREOGRAPHIC PROJECTION OF PLANES IN THE ISOMETRIC SYSTEM. PLANE OF PROJECTION = (001) .

Owing to the fourfold symmetry of the original projection, the twin structures corresponding to the two remaining zones may be obtained by reorienting the projections shown in Figs. 8 and 9.

Thus the poles (211) in the first zone and $(\bar{1}21)$ in one of the remaining zones occupy similar positions in adjacent quadrants of Fig. 7 so that the projection of the first twin (Fig. 8) when turned 90° counter-clockwise represents the structure of this other twin, disregarding the signs carried by the indices of all planes.

Similarly, the structure of the last twin may be obtained by turning the projection shown in Fig. 9, in this case 90° clockwise, so that the

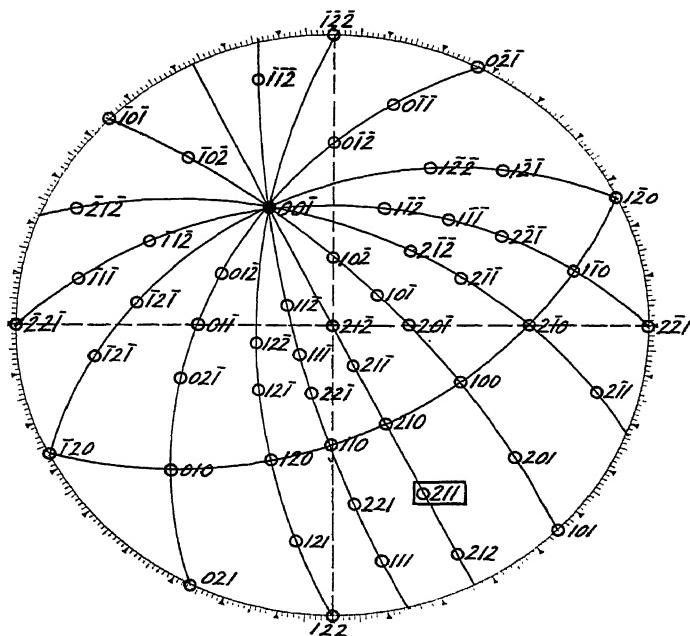


FIG. 8.—STEREOGRAPHIC PROJECTION OF PLANES IN THE ISOMETRIC SYSTEM AFTER TWINNING ALONG THE PLANE (211). PLANE OF PROJECTION = ORIGINAL PLANE (001).

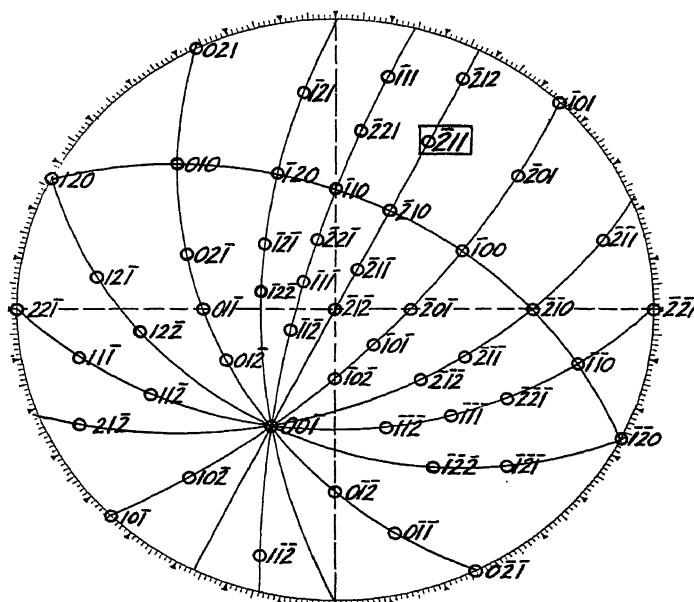


FIG. 9.—STEREOGRAPHIC PROJECTION OF PLANES IN THE ISOMETRIC SYSTEM AFTER TWINNING ALONG THE PLANE $(\bar{2}11)$. PLANE OF PROJECTION = ORIGINAL PLANE (001) .

pole of the original twinning plane ($\bar{2}11$) coincides with the pole of a new twinning plane (121).

EINFACHE SCHIEBUNG IN FERRITE AS OBSERVED BY O. MÜGGE IN 1899

If a sphere circumscribed by a cube is deformed by equal amounts of compression on one pair and tension on the other pair of vertical surfaces it will take the form of an ellipsoid of equal volume, with the vertical axis, along which no strain has occurred, equal to the diameter of the sphere and two circular cross-sectional planes of maximum tangential strain also of this diameter.¹⁴ Thus, all points and directions in these planes will appear to have suffered no change as a result of the deformation.

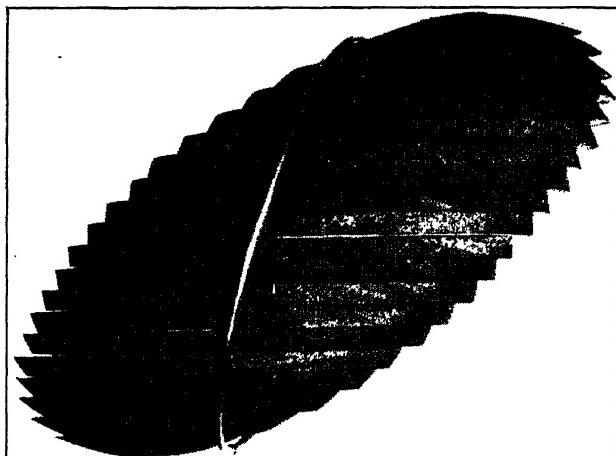


FIG. 10.—DEFORMATION OF A SPHERE BY SLIDING PARALLEL SECTIONS EQUAL DISTANCES OVER ONE ANOTHER (*Einfache Schiebung*).

The same strain ellipsoid may be produced by a totally different kind of deformation; namely, by sliding the planes which lie parallel to one of these circular cross-sections equal distances over one another, as represented on a gross scale in Fig. 10. A ring marks the position of the second circular cross-section.

This is the mechanism which under the title *Einfache Schiebung* has been introduced as a precise characterization of mechanical twinning. With one of the circular cross-sectional planes in stationary position as a twinning plane, the *Schiebung* (*s*) is the distance that a plane one unit distant from the twinning plane must move in order to bring about a reorientation of the crystal planes in conformity with the twinning law. It is important to note that the circular cross-sectional planes, commonly

¹⁴ For a full discussion of this subject, see P. Niggli: *Lehrbuch der Mineralogie*, 2d Ed., 289 et seq. 1924.

designated k_1 and k_2 , do not change form or indices as a result of the transformation. There are simple geometrical relations between s , the angle between k_1 and k_2 , and the axes of the deformational ellipsoid.

In practice, these fundamental values may be calculated from observation of the angles between known surface planes and parts of the same surface after alteration by twinning. Mügge made his observations on cubic cleavage planes in a "block of soft iron." The Neumann bands run parallel either to the cube face diagonals or to lines drawn from the corners to the centers of opposite sides. A band twinned along the (112) plane would represent the first variety when viewed in the (001) plane. The average angle between the surfaces of such bands formed spon-

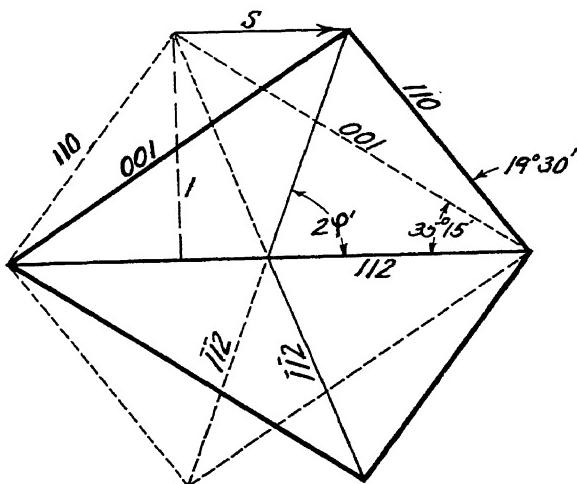


FIG. 11.—DIAGRAM OF TWINNING BY *Einfache Schiebung* IN IRON.

taneously during cleavage and the cleavage surface on which they were observed was $18^{\circ}11'$.

The significance of this result will be seen in the diagram, Fig. 11, which represents the *Schiebung* or movement required to twin a unit cube along a (112) plane and the consequent transformation of planes as it appears on a cross-section normal to the twinning plane and including the direction of *Schiebung*, s .

The central horizontal line marked 112 represents the twinning plane and the direction of translation. The lower heavy triangle is a section through the untwinned half of the cube and the half lying above the twinning plane is continued with dotted lines. If, now, the upper left-hand corner is pushed along a distance s parallel to 112, the contour of the upper half must change to the twin configuration indicated by the heavy triangle, which might also be produced by the customary 180° rotation around an axis perpendicular to the twinning plane. If the

distance between s and 112 is greater than the spacing between adjacent (112) planes the intervening atoms will advance in proportion to their distance from the twinning plane. It is evident that the *Schiebung* just described moves the (110) plane of the original crystal through a certain angle into the (001) plane of the twin and similarly the (001) plane over into the (110) plane.

This is the angle measured by Mügge in the case of the diagonal bands. His value is about 1.25° less than the true value, $19^\circ 30'$ (within a few seconds) shown by this construction. The value of s and the angle (2φ) between 112 and $\bar{1}\bar{1}2$, representing k_1 and k_2 of the deformational ellipsoid, may be taken from the figure:

$$s = 0.707, \text{ or } a_o \cdot \frac{\sqrt{3}}{6}, \text{ expressed in \AA ngströms and } 2\varphi = 70^\circ 30'.$$

Mügge also measured angles between other surfaces of the same lamellae, which should correspond to the indices (112) and (112) and the cleavage surfaces (100) and (010), respectively, on which they appeared. In this case he obtained an average value of $18^\circ 19'$ using original cleavages and $15^\circ 34'$ using repolished surfaces on which the bands were produced by subsequent light hammering. The first average is $36'$ greater and the second average $2^\circ 9'$ less than the theoretical angle between these planes, $17^\circ 43'$.

Although these experiments were not sufficiently accurate to give a clear distinction between the angles at the cleavage surfaces, the results taken in connection with the qualitative evidence as to location and relationship of the different lamellae seem to justify Mügge's conclusions, which may be summarized in the form of his equations expressing the relation between the indices, h_1, h_2, h_3 , of a plane before and, h_1^1, h_2^1, h_3^1 , after the transformation (twinning plane = 112):

$$\begin{aligned} h_1^1 &= -h_1 + h_2 + h_3 \\ h_2^1 &= h_1 - h_2 + h_3 \\ h_3^1 &= 2(h_1 + h_2). \end{aligned}$$

THE NEW EXPERIMENTS

The material used was silicon ferrite in strips about $5/8$ in. wide and 0.025 in. thick, very kindly furnished in nearly single-crystal form by W. E. Ruder, of the General Electric Co. The following analysis was obtained from one strip which contained the crystal used in most of the X-ray work: silicon, 3.78; carbon 0.044; manganese, less than 0.01.

Neumann bands were produced in this material by bending, stretching, rolling and hammering. Their appearance was accompanied by a crackling sound similar to the tin or zinc "cry." In no case, however, was it possible to produce this structural transformation in any con-

siderable volume of the material. Single-crystal strips with cubic planes very nearly parallel to the surface crackled noticeably when pinched between rolls but produced only a few bands. When rolled on dodecahedral planes virtually all of the deformation occurred by a quiet slipping process. Iron, therefore, behaves quite differently from zinc, which may be twinned quantitatively¹⁵ by rolling.

We desired to analyze the structure of the bands by X-ray diffraction according to the Laue method, which had been found adaptable in the zinc investigation. Obviously the structure under investigation should be effectively concentrated in the region traversed by the X-ray beam, and general deformation, which makes it difficult to interpret the diffraction spots, owing to asterism, should be avoided as far as possible. The best results were obtained by clamping the strip between heavy strips

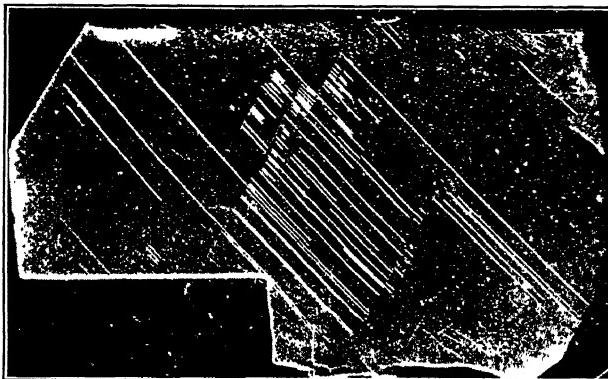


FIG. 12.—NEUMANN BANDS ON ONE SURFACE OF CRYSTAL USED IN X-RAY EXPERIMENTS.
X 5.

of brass and hammering the assembly edgewise. Most of the plastic deformation was confined to the edge but the bands, which were never more than 0.02 mm. wide, spread rather generally over both surfaces and frequently passed entirely through the crystal.

One surface is shown at low magnification in Fig. 12. The notch at the left represents a piece which broke away along perfect cubic cleavages during the hammering. With the aid of these cleavage surfaces it was comparatively easy to determine the orientation of the crystal. The two sets of bands shown in this photograph were also visible in the long cleavage surface at the bottom.

Angular measurements made on this crystal are summarized in the sketch at the left in Fig. 13. The stereographic projection at the right shows the poles of the two twinning planes, *A* and *B*, the cleavage planes,

¹⁵ C. H. Mathewson: *Op. cit.*

F and F' , and the plane (001), with the surface of the crystal (S) as the original plane of projection and the edge joining F and S as the X axis.

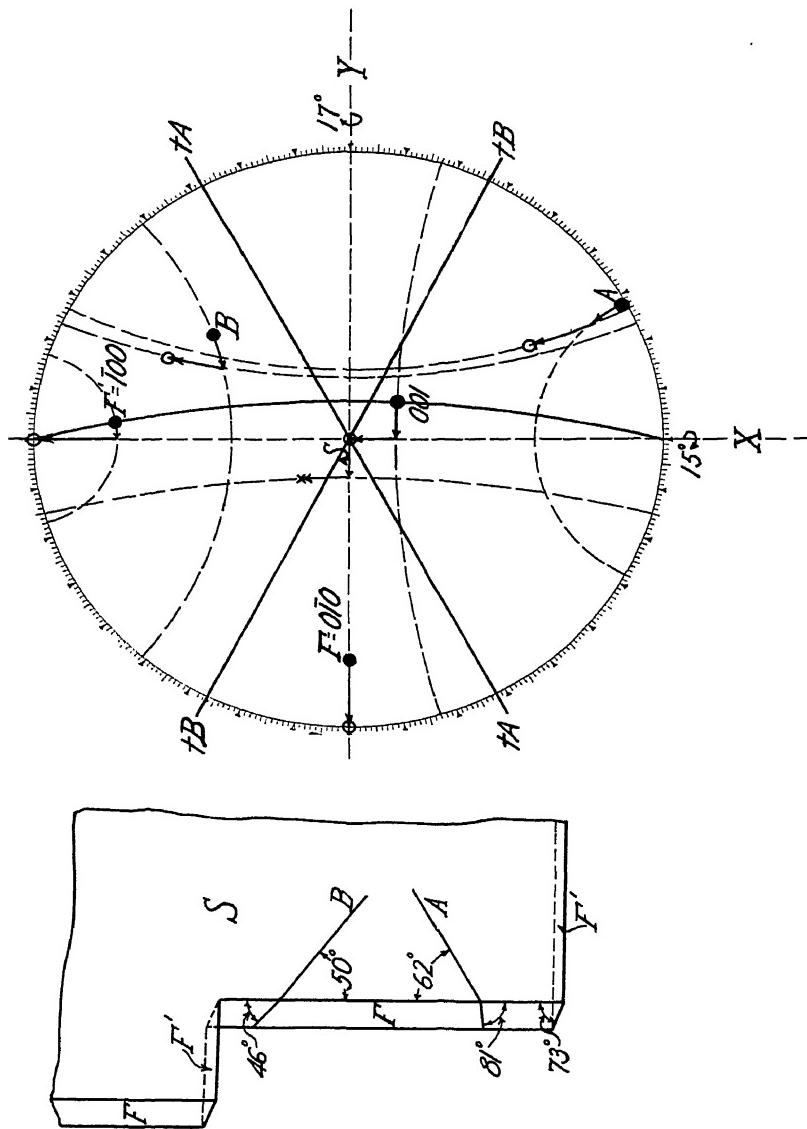


FIG. 13.—STEREOPGRAPHIC PROJECTION OF TWINNING PLANES AND SURFACES OF CRYSTAL USED IN X-RAY EXPERIMENTS.

A construction for locating the poles of intersecting planes such as A and B when the plane angles at the edge are known has been described by A. J. Phillips.¹⁶ The dihedral angle between F and S (not shown

¹⁶ A. J. Phillips: Twinning in Copper and Brass. *Proc. Inst. Met. Div.* (1928) 429.

in the sketch) was found to be about 75° , so that the great circle containing F is inclined 15° to the vertical with its pole at $F = (010)$. The pole of $F' = (\bar{1}00)$ must lie on the great circle with pole at F and was located 17° up from the horizontal or 73° down from the vertical plane. The pole of (001) must occur 90° farther along in the same zone.

If the crystal is now rotated 15° around the edge $F-S$, or X axis, the poles will all move, as shown by the arrows, in vertical small circles and F will reach the customary position of $(0\bar{1}0)$. Following this, a rotation of 17° around the Y axis will cause all poles to move in a corresponding set of small circles into their customary positions with the plane (001) at the center of the projection. The traces of the twinning planes A and B on (001) are now tA and tB (90° to the lines joining the poles with the center), which come out 26° or 27° to the cleavage F' . This identifies them as bands whose traces in a cubic plane are parallel to lines drawn from the corner to an opposite side. It is now clear that the A and B bands are parallel to the respective planes (211) and $(\bar{2}11)$, which lie in different twinning zones, as pointed out in the discussion of Fig. 7. They should, therefore, be structurally dissimilar.

A spot just below the upper central V in Fig. 12 was selected for X-ray examination. A and B bands were present in approximately equal quantities on one side of the specimen, with B bands somewhat in excess on the other side. It is probable that less than 15 per cent. of the crystal radiated by the X-ray beam was in the form of twin lamellae.

The crystal was turned in front of the beam exactly as described in Fig. 13 so as to bring the (001) plane normal to the rays and produce from the original crystal a simple Laue pattern of fourfold symmetry. The experiments were performed in the General Electric diffraction apparatus, using general radiation from a molybdenum target passed through a pin-hole element of the new slit system supplied as part of the equipment. Fairly satisfactory simple patterns representing the structure of the original crystal were obtained after an exposure of about 16 hr. with a tube current of 19 to 21 ma. and a primary voltage of 90, but the production of satisfactory diffraction spots from the twin bands required exposures three or four times as long.¹⁷

Only one of the twin spots was of sufficient intensity to show clearly in the reproduction, Fig. 14, of the best pattern obtained. This is the small, but rather bright spot at the lower right halfway between the center

¹⁷ Several additional crystals were investigated, one in the original condition and the others twinned by various forms of manipulation. The beam in most cases was normal to (001) in the original crystal but one crystal was oriented to bring a cubic plane in a predominant twin normal to the beam. In all cases the large majority of the diffraction spots came from planes in the original crystal but the presence of Neumann lamellae was always revealed after a lengthy exposure by a few spots which could be explained only on the assumption of twinning as set forth in these pages.

and the inner group of very large and bright spots. The elongated spot very near the bright center came from (110) planes of the original crystal, originally parallel to the beam but now tilted (or crumpled) as much as 4° to 5° as a result of the hammering required to produce the Neumann bands.

A gnomonic projection giving the identification of all spots observed on the film is shown in Fig. 15. It was made from a positive print of the original negative. The indices shown with heavy figures represent the

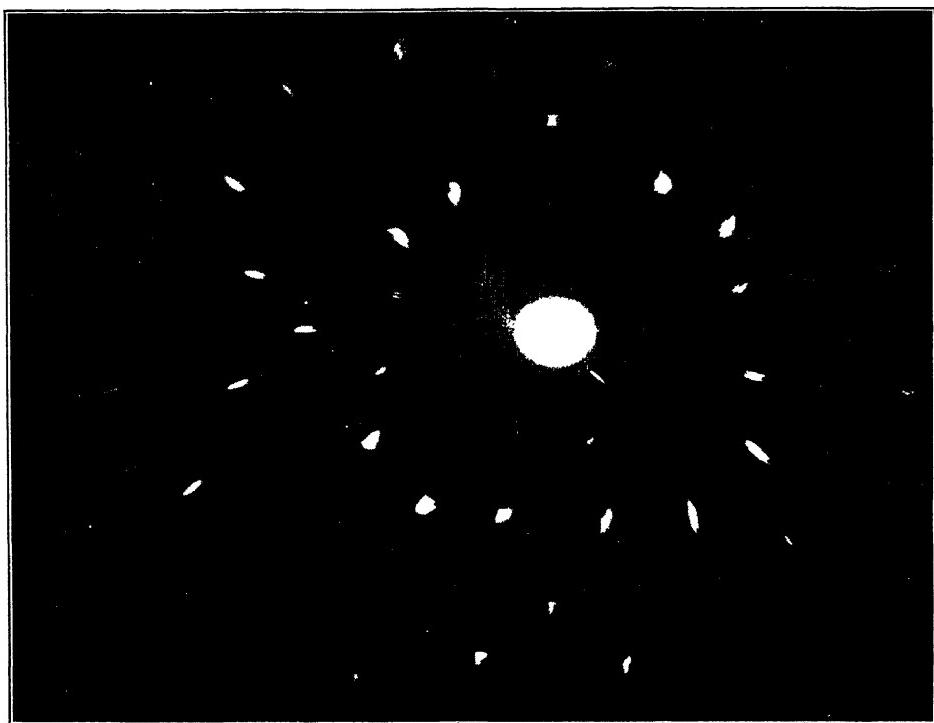


FIG. 14.—LAUE PATTERN OF CRYSTAL SHOWN IN FIG. 12.

planes of form {321} and {411} which are responsible for the inner grouping of bright spots in Fig. 14. The (4 $\bar{1}$ 1) plane is not included, as the adjustment of the crystal to the X-ray beam deviated sufficiently from the intended position, beam \perp (001), to bring the angle θ for this plane outside of the reflection range for wave lengths encountered under the conditions of operating the tube. Although this plane may be replaced by a plane of form {110} in one of the four possible twins, thus permitting reflection with longer wave lengths, this particular twin was not available in the present case. The (411) plane is even less favorably

located for reflection and the faint spot actually obtained is therefore attributed to reflection from $(0\bar{1}1)$ planes of twin band A which are found in the same position.

The reflection conditions encountered with these different planes of form $\{411\}$, which differ slightly in their angle of inclination to the X-ray beam, when expressed in the fundamental equation $n\lambda = 2d \sin \theta$, indi-

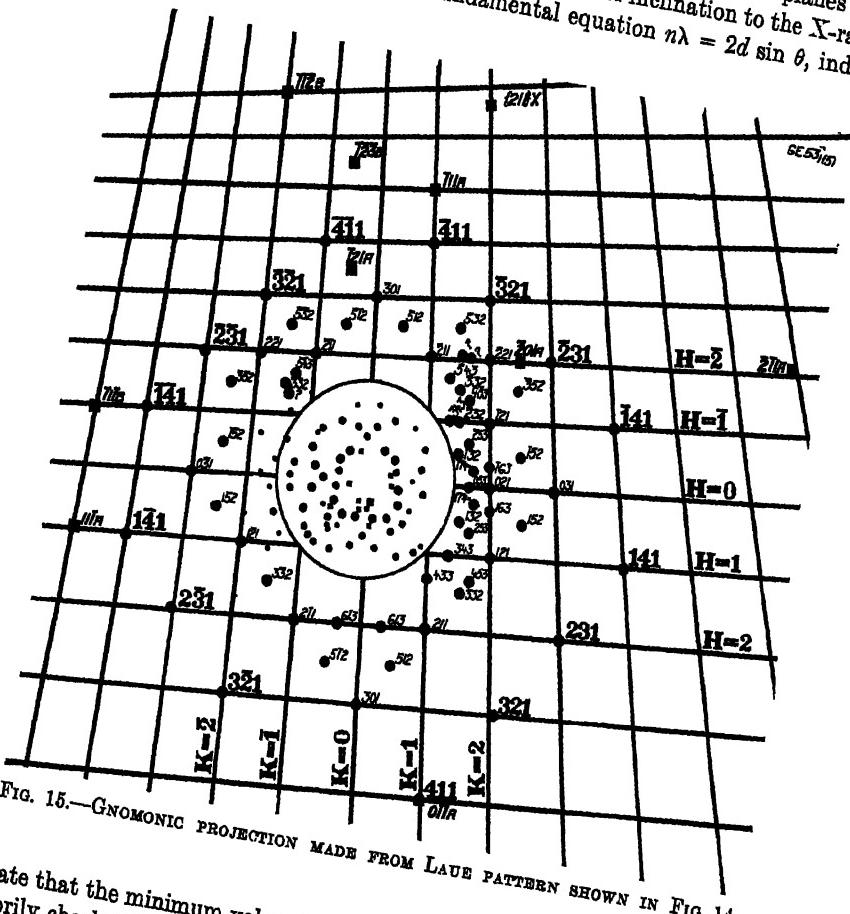


FIG. 15.—GNOMONIC PROJECTION MADE FROM LAUE PATTERN SHOWN IN FIG. 14.

cate that the minimum value of $n\lambda$ was about 0.27 \AA . This was satisfactorily checked in other ways.

The spots which we have traced to the Neumann bands are shown as squares in the projection, Fig. 15, with indices and the letter A or B denoting a band lying parallel to the $(\bar{2}11)$ or (211) plane, respectively. One spot, designated $\{211\} X$, might have come from planes of form $\{211\}$ in inconspicuous lamellae parallel to any one of the three twinning planes, $(\bar{1}21)$, (112) or $(\bar{2}11)$.

Table 1 gives indices referred both to the axes of the original crystal and the axes in twin position,¹⁸ along with the wave lengths that would be required for reflection in both cases.

TABLE 1.—*Reflection Data from Planes in Neumann Bands*

Indices Based on Axes		$n\lambda$ in Ångströms Referred to Planes	
Of Original Crystal	In Twin Position	Of Original Crystal	In Twin Position
511	111 A	0.120	0.360
721	{211} X	0.128	0.386
452	201 A	0.131	0.391
271	211 A	0.101	0.318
411	011 A	0.271	1.090
(411)	Not observed	0.273	
151	111 A	0.111	0.333
151	111 B	0.116	0.350
721	112 B	0.129	0.388
712	121 A	0.236	0.709
1112	123 B	0.105	0.384

It is quite clear that only one of the 10 diffraction spots referred to the Neumann bands could have come from planes in the original crystal as this would have required the action of waves far below the limit of the short wave length. This exceptional spot, the fifth in Table 1, may have been produced by the plane (011) of band A ($\lambda = 0.363$ for reflection of third order) acting in conjunction with the plane (411) of the original crystal ($\lambda = 0.271$).

The spot corresponding to the plane (112) of band B and the wave length $\lambda = 0.388$ (the only one which can be seen in the printed pattern) was by far the most intense of all spots from twin planes. It is of interest that the brilliant spots from planes of form {321} in the original crystal correspond to $n\lambda$ values between 0.35 and 0.46 Å. In general, we have considered it inadvisable to study the intensity effects owing to irregular distribution of the twin lamellae and high absorption in the predominant volume of untwinned crystal.

¹⁸ The indices of a plane in the twin band may be obtained from the indices of a plane of the original crystal in the same position by using the following equations of transformation:

$$\left. \begin{aligned} h_t &= h_o - 2k_o - 2l_o \\ k_t &= -2h_o - 2k_o + l_o \\ l_t &= -2h_o + k_o - 2l_o \end{aligned} \right\} \text{for band } A \text{ parallel to } (\bar{2}11)$$

and

$$\left. \begin{aligned} h_t &= h_o + 2k_o + 2l_o \\ k_t &= 2h_o - 2k_o + l_o \\ l_t &= 2h_o + k_o - 2l_o \end{aligned} \right\} \text{for band } B \text{ parallel to } (211)$$

Supplementing the formal presentation of these data, we have prepared a sketch, Fig. 16, in which the reflections from two planes in each of the twin bands may be visualized in relation to the original crystal. The specimen with characteristic angles, planes and bands and a diagram

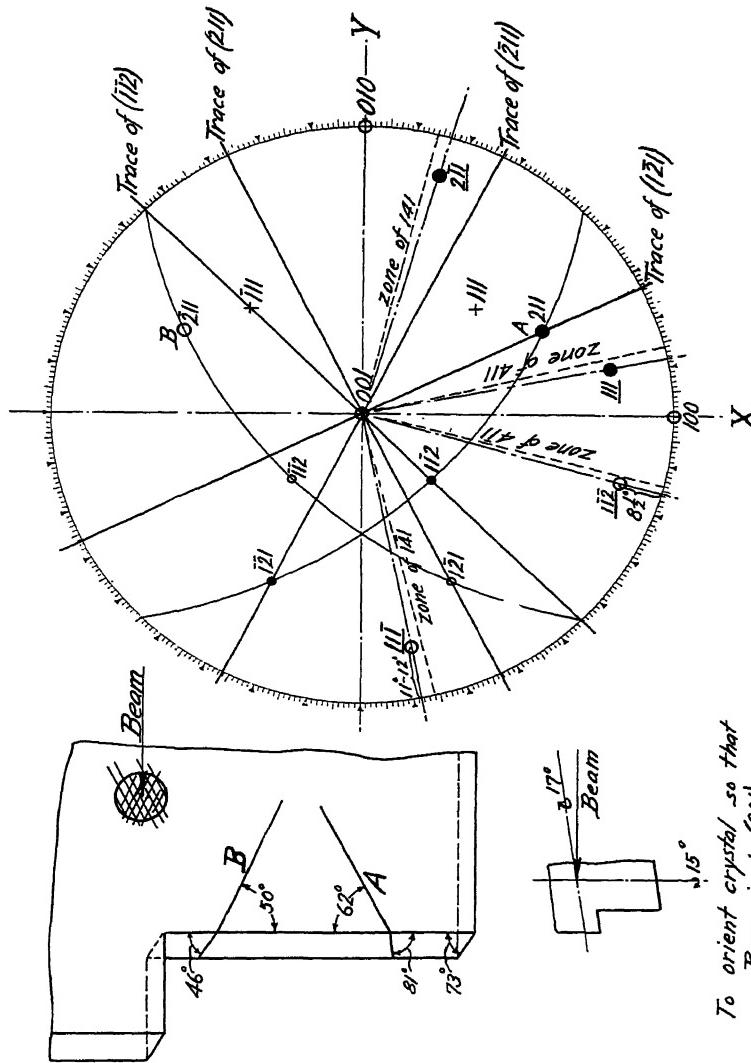


FIG. 16.—STEREOGRAPHIC PROJECTION ON THE (001) PLANE OF THE ORIGINAL CRYSTAL OF THE PRINCIPAL TWINNING PLANES A AND B AND IMPORTANT REFLECTING PLANES IN THE TWIN LAMELLAE.

representing its orientation in front of the beam are shown at the left. A stereographic projection in the cubic plane which lies nearest the visible surface is shown at the right, with the point of sight on the other side of the crystal and below the projection as it appears in the customary horizontal position. Band *B* is parallel to the twinning plane ($\bar{2}11$) whose

pole is indicated by a hollow circle at $B\bar{2}11$. Referring to the projection of the planes in general after twinning around $(\bar{2}11)$, previously given in Fig. 9, it is seen that the planes $(1\bar{1}\bar{2})$ and $(11\bar{1})$ are located close to the positions designated by open circles in Fig. 16, which were determined directly from spots on the Laue pattern. Thus a line through the center of Fig. 14 and the small bright spot about $\frac{3}{4}$ in. below at the right establishes a radial zone less than 2° clockwise from a similar radial zone passing through the center of the nearest large spot, which represents the $(\bar{4}11)$ plane of the original crystal in the gnomonic projection of Fig. 15, or the $(4\bar{1}1)$ plane according to the projection scheme of Fig. 16.¹⁹ Moreover, the angular distance (2θ) from the center to the small spot corresponds to reflection from a plane (5 cm. from the film) inclined (θ) 8.5° to the X-ray beam. These conditions are met by the plane $(1\bar{1}\bar{2})$ of the B twin whose pole is shown 8.5° up from the horizontal in the appropriate zone of Fig. 16. Another spot was found to meet the conditions of reflection from the plane $(11\bar{1})$ and its pole is located 11° to 12° up from the horizontal in another radial zone close to a similar zone through the pole of the $(\bar{4}11)$ plane.

It should be clear from the earlier discussion that twin bands parallel to two other twinning planes, namely $(\bar{1}\bar{1}2)$ and $(1\bar{2}1)$ would also have planes of form $\{211\}$ and $\{111\}$ in position for reflection as described above. The poles of the three related twinning planes are connected by a zone circle in Fig. 16 with its pole at (111) . The traces of all three twinning planes in the plane of the projection are also clearly indicated.

Precisely the same considerations apply to the location of the poles of the two reflecting planes in the A twin, in this case designated by black circles, by analyzing the spots found in the Laue pattern.

ACKNOWLEDGMENTS

In conclusion, we wish to acknowledge our indebtedness to Prof. L. W. McKeehan, who has critically reviewed this manuscript, and to Dr. Albert J. Phillips, who prepared much of the illustrative material and assisted in the general discussion of the problem.

DISCUSSION

L. W. MCKEEHAN, New Haven, Conn.—The author mentions a recent paper on the explanation of slip in ferrite, and since one of the figures which he has given is easily used in explaining the type of slip that the author of that paper now proposes, and

¹⁹ It should be observed in comparing these stereographic projections with the Laue pattern, Fig. 14 and center of Fig. 15, that the latter is a printed positive which must be viewed as a negative to give the right relation between spots and planes according to the reflection scheme of Fig. 16. The indices of the same planes shown in Figs. 15 and 16 are therefore different. They may be made alike by changing the first sign in every case.

since it is an intermediate type between two preceding views, I thought it might be interesting just to mention what it comes to.

In Fig. 7 the lines to which Professor Mathewson has referred are the arcs extending across the circle. Each has on it the poles of three planes of the form {211} which are competent to serve either for slip or twinning. Besides that, there are a number of other planes the poles of which fall on these arcs. These are planes of the form {110} and planes of the form {321}.

Gough²⁰ has said that all these three types of planes are sometimes slip planes in iron, whereas one of the previous views was that only planes of the form {211} were competent to produce slip or competent to act as slip planes; and the other view, that of Taylor and Elam, was that any plane at all of which the pole would fall upon one of the arcs in question might act as a slip plane or be at least a plane tangent to the columns which the latter authors referred to in their columnar theory of slipping.

The latest view, therefore, is intermediate between the extreme view that only planes of form {211} can serve for slip and the view that any plane whatever containing the line [111], which is common to all these planes, might so serve. Since there are so many of them, 48 altogether, with four possible directions of slip, the elucidation of the exact planes that do the slipping is a complicated job, even more complicated than what Professor Mathewson has outlined.

²⁰ H. Gough: The Behaviour of a Single Crystal of α -Iron subjected to Alternating Torsional Stresses. *Proc. Roy. Soc.* (1928) 118A, 498.

Blast-furnace Operations and the Character of Pig Iron and Castings

ROUND TABLE CONFERENCE

(New York Meeting, February, 1928)

THE Iron and Steel Committee of the American Institute of Mining and Metallurgical Engineers held a joint session with the American Foundrymen's Association during the Annual Meeting of the Institute in February, 1928, for the purpose of discussing blast-furnace operations and the character of pig iron and castings. Dr. Richard Moldenke presided.

R. H. Sweetser, who was named on the program as the presiding officer of the session, was unable to be present, but sent a letter in which he said:

"The meeting we had here last year and the meeting held in Chicago last June showed a desire on the part of blast-furnace men and users of pig iron to get the facts regarding the influence on castings made from pig iron produced in blast furnaces under varying conditions of temperature, mixture and local furnace operations. It has been my hope that at this Round Table we might be able to formulate a series of tests that would give us the desired information.

"Several independent blast-furnace investigations have been, and still are being, carried on in different sections of the country. The furnaces investigated include a southern furnace, a middle-west furnace, a western furnace and a Chicago district furnace. The results so far show distinct characteristics for each of the four furnaces. It is possible that a furnace in the eastern part of the United States would be different from all the others.

"It is hoped that a plan of action can be worked out at your meeting today whereby the U. S. Bureau of Mines will be able to carry on more extensive work in connection with the research departments of the different iron and steel companies and the big consumers of pig iron.

"No one group can get all of the information but if the different investigations can be coordinated it will be possible for us to draw conclusions regarding the effects of varying conditions in blast-furnace practice on the pig iron produced and the castings made therefrom."

DISCUSSION

R. MOLDENKE, Watchung, N. J.—I was across the water this summer and saw some of those interested in an investigation of this kind. They told me that in Germany, where they had a joint committee of blast-furnace operators and foundry-

men, they had sent pig iron made in various ways to two large foundries that I knew very well. The results were absolutely worthless and they stopped the investigation altogether. They had followed what I had written on this matter in the mining and foundrymen's meetings, and in which I held that the solution would be found in devising some test on remelted pig iron.

The suggestion I made was to take the samples of the pig and put them into a resistance electric furnace and melt under conditions as normal as would be the case in the foundry, all melts to be of the same temperature. Then pour into bars and submit it to strength and shock tests and perhaps a number of other tests to learn the physical properties of the iron. Nothing came of it here, but the German foundrymen took it up, bought a resistance furnace and at that time were undecided whether to put it in the hands of their committee or into the Düsseldorf plant of the Kaiser Wilhelm Institut für Eisenkunde. This would give physical results for pig iron remelted under standard conditions and these physical results under similar chemical analyses could be compared with each other, which would gradually establish a series of tables and furnish useful information for specification purposes.

We have been talking about this off and on a good deal but you cannot readily put your finger on the solution. Every man has his own way of doing things. The iron I want is not the iron the other man wants, and if we can get something done here today I will be very much surprised. My personal feeling is that we cannot get anywhere by mere cooperation of furnace and foundrymen; we must have a test on the pig iron itself.

C. H. HERTY, JR., Pittsburgh, Pa.—I am not sure about the foundry and blast-furnace work. We are beginning to do a little work on cupola iron that various foundries around Pittsburgh bring to us. We have only one direct comparison so far between a good foundry iron and a bad foundry iron and I rather imagine the bad foundry iron was the worst they ever got. It had a low tensile strength and was very blowy and it was interesting to find in that iron that there was 0.8 per cent. of silica, SiO_2 , and it was very highly oxidized. The normal good foundry iron we have obtained runs about 0.01 to 0.02 silica. It is very well deoxidized, that is the main difference.

We are continuing, more or less sporadically, by getting samples in from various foundries, but we found a very interesting thing in connection with open hearth tests that we ran last February and that is that in the open hearth high combined carbon has no effect whatsoever on the quality of the open hearth steel.

On the foundry iron we are just beginning to get started and we do it more or less in spare time and in connection with other work, not as a major problem in itself.

R. MOLDENKE.—It is rather news to foundrymen that you get silicon oxidized to SiO_2 in large quantities in molten iron.

C. H. HERTY, JR.—This was from the cupola. I might mention in connection with the 0.8 silica cupola iron, with good iron the silicates run 0.01 to 0.02 per cent. and that the average (when it was not either very bad or good) of blast-furnace iron was about 0.02. Good cupola ran 0.01 to 0.02 and the poor cupola iron ran 0.8, or about 40 to 80 times as high in silica as the good cupola iron and the blast-furnace iron.

GOOD IRON VERSUS BAD IRON

R. MOLDENKE.—You make a bold statement, "good iron and bad iron." Will you tell us what that means?

C. H. HERTY, JR.—As far as I have been able to get from last year's suggestions, bad furnace iron is anything that makes a casting bad.

R. MOLDENKE.—I am afraid that will not answer. When you come to think of it, what ground has the foundryman to say, "I have some bad pig iron?" The only way he knows, so far as I can see (and that is why the German experiments failed), is that he may run along six months with the same analysis of iron, the same fuel and practice, and satisfactory results; then suddenly his castings become unsatisfactory. He has not changed his practice or analysis but something has happened somewhere. He begins to look around, changes his pig irons and good results come back. Naturally, the thought comes into his mind, "It was bad pig iron."

It is difficult to prove these things. What we must try to do is to make so simple and so easy a test that the foundryman does not have to run two or three months of bad castings before he finds out whether his pig iron was at fault. The foundry demands that molten iron shall have what is called "life." This means that it can be held 15 or 20 min. before pouring.

C. H. HERTY, JR.—The logical way to start on the problem is in the foundry and not at the blast furnace. In other words, if a foundryman likes one kind and not another, obviously the thing to do is to find out the real difference. There is some difference; there is no question about that. When we say that the analysis is the same, we mean that the carbon, manganese, and so forth are the same, but that is not by any means the whole story.

My belief is that we should start at the foundry and have a man who is supported by the foundrymen's association and the blast-furnace men, preferably both, to follow the practice on pig iron coming in, castings being made, kind of pig iron the foundryman thinks he is getting (lively or dead) and at the end of two or three months pick certain pig irons and castings and go to work on the ones that gave good castings and those that gave bad castings; not to try to get the effect of scrap, but to start back where the product is being run off and analyze it to the last drop; also the materials that went into its making, to the very last drop. In other words, diagnose the trouble, find where it is and then work back into the pig iron rather than start with the pig iron and try to make different grades of castings with that.

We had an interesting case of that in the open-hearth work. It was disastrous in one way and illuminating in another. We tried to make the kind of pig iron that the open-hearth people said gave bad steel. We ran 20 per cent. silicon in the iron for three casts, but the steel was as pretty as anything you ever saw. It was low-carbon steel, which may have covered up some of the poor quality of the iron. When we threw the blast furnace off we did not get quite the condition that everybody was looking for.

R. MOLDENKE.—I think what runs through the mind of the foundryman is not to find a reason for a particular lost casting but for a general deterioration in the product. Say you desire a certain deflection, bending strength, or tensile strength in the iron, and this gradually gets lower. The castings are just the same in appearance but you know that when they go into service they will break much sooner; so it is not a case of a bad casting or a good casting that you pick out of the pile, but the run of the foundry product as it goes along.

C. H. HERTY, JR.—That is what I am talking about. When the man stays on the job three or four months, he cannot go one day and pick a casting here and there, but will keep his samples of every cast period, even if it takes a warehouse to hold them, all labeled correctly, and when he comes to those giving the wrong results, compare them with those giving the right results and go back to the iron in the castings, and further, if possible. It may not be necessary to go further back.

R. MOLDENKE.—You cannot do justice to the work in one place but may have to go to a dozen; to places where all the different classes of irons used in the foundry are melted.

H. BORNSTEIN, Moline, Ill. (written discussion).—The gray-iron foundry industry is confronted with many difficulties on account of the complexity of its product. Not the least of these is the lack of definition of the difficulties themselves. The A. F. A. committee, having come to the realization of the necessity for definition of the various elements of the problem, has reached the conclusion that progress may be expected only after these definitions have been arrived at. Therefore the committee proposes to attempt the formulation of a series of specific problems, the answers to which will at least assist in the establishment of means of measuring qualities which determine the usefulness of the product cast iron. When these means of measuring qualities have been determined, there is the immediate opportunity to determine the influence of variables in raw material and practice upon the output.

We have every confidence that when the problem has been thus defined there will be found the active sympathetic cooperation among the interests involved in the prosecution of the research.

DEFINITION OF TERMS

J. A. CAPP, Schenectady, N. Y.—We can go on talking indefinitely unless we develop facts upon which we can first agree. We talk about a bad casting. There probably are as many kinds of bad castings as there are castings made. What is a bad casting to one man may be an ideal casting to another. There is no yardstick by which badness or goodness in any single intrinsic property can be measured. We are talking glittering generalities when we talk without definition. One man's problem is that a casting does not machine as well as another casting, yet it may be made nominally in the same way by supposedly the same composition of pig iron, by as nearly the same cupola practice as he can determine, but when he tells you how badly it machines he says only "badly."

You can reason by analogy that does not apply so comfortably to cast iron as it does to other things. We find in steel, for instance, that it is quite common for a man to tell us a casting is too hard or a forging is too hard to machine. Half of the time it is not too hard, it is too soft; so soft it drags and the cutting tool tears the material rather than cuts it.

I know of a case of cast iron that was said to be too soft, yet, recognizing the fact that it gave tremendous difficulty in machining I discovered that it was merely due to its being too fine grained for the kind of operation to be performed. When we changed the method of machining to the more expensive one of grinding, it was beautiful metal. Instead of being soft, and therefore open grained, it was too hard.

There was no measuring stick applied there. There was none available. When does an iron become too hard to be machined by a certain type of tool? Is the answer a change of the iron or a change of the tool? They are both legitimate answers.

We say to the blast-furnace people, "You have given us bad pig iron;" they resent it and tell us about the good quality of the pig iron and ask us to prove it bad. We cannot do it because we do not know what is the matter with the casting. We have not measured it in any determinable terms and until we do determine on terms, methods of measuring intrinsic quality, how can we hope for a remedy for our ills?

The standard test bar that we pour tells us something about the character of the iron in certain directions but not in all directions. The great iron foundry industry covers a tremendously wide field. There are many, many ways of looking at goodness or excellence in iron castings. It is hopeless to expect one measure of that excellence. There may be a measure of ability to make sharp, clean-cut, accurate castings. There may be an entirely different measure of strength in castings, a measure that will enable the poor duffer in the laboratory to tell the designing engineer what he wants to know, how strong is his casting or how resistant to the stresses of service is his casting.

Today we can tell him that his test bar has so much transverse strength and deflects so much but none of us dares tell him how strong the casting is, which he needs to know. The test bar tells us something of the composition of the iron to the extent to which we determine composition. Quite possibly in the case Dr. Herty cited they measured silicon and omitted silica. They had the right amount of silicon perhaps, but it was not all there in the form in which we expect silicon to be present in cast iron. Some of it got tangled up somewhere, through the cupola probably.

How often are we sure that all the elements that we customarily measure in pig iron or cast iron are combined with one another in the same way? How much do we know about the persistence of that mode of combination as it may exist in the pig iron through its melting operation in the cupola? How much do we know about how the changes may take place in the cupola, changing those forms of combination? Is the silicon all there as an iron silicide? Is it there some other way? Is the manganese there? How? With iron? Is it a compound of manganese with something else? How persistent is that combination? What is its influence? How can you measure the influence and determine it?

We can talk almost indefinitely until we develop facts. If we will deliberately set out to try to establish what are the really useful properties of cast iron, define them in some way, we will find a way to measure them, and when we have found the way to define them and then the way to measure them, the determining of the influence of variables upon them is not going to be a particularly difficult problem.

R. MOLDENKE.—Suppose we take an iron of a given composition and melt it with a superheat of 2350° to 2450° F., pour test bars and obtain normal strengths. If we heat up more of this molten iron—say to 2850° F.—and pour test bars, these will be nearly double as strong. What is the use of an investigation if that can happen? The question of degree of superheat is an all-important factor. There is in the air a question of establishing an American Institute for Cast Iron Research, and this would be a good question to work upon in such an event.

STUDY OF LIQUID CAST IRON

A. L. FEILD, New York, N. Y.—It is certain that the properties of liquid cast iron are defined entirely by temperature and composition, if gases and dissolved oxides are included, regardless of what raw material you start from. It seems to me that the material to study is liquid cast iron. If possible, the iron should be quenched so rapidly from the liquid state—using a water-cooled copper or liquid-air chill—that a picture of the liquid cast iron at the temperature in question will be retained. The question of what happens afterwards in practice is controlled entirely by mold design.

R. MOLDENKE.—That is very interesting. Many casting problems have been touched upon. For instance (Piwowarsky told me this) if you melt the iron to a very high degree of superheat and thus dissolve the nuclei of graphite ordinarily present, and for cooling the ladle put in a piece of sprue, you introduce nuclei of graphite again and spoil the benefit of the high superheat.

If the foundryman charges ferrosilicon and ferromanganese in the cupola he would have a heavy oxidation to contend with and he would get no satisfactory result, but take the ferromanganese and the ferrosilicon and put with them 15 per cent. of Portland cement to make a briquette of the material; the cement will set and make a stone. Put the briquettes on a core oven to warm for a week or so, and dry out the moisture and then charge. The briquettes are distributed uniformly and the ferrosilicon and ferromanganese are not oxidized a particle till it gets in the melting zone and you can have only the ordinary oxidation occurring there.

H. BORNSTEIN.—This has nothing to do with the subject of pig iron, but I might say that at Moline we followed out the recommendations of the International Nickel Co., which means the introduction of a 96 per cent. steel charge, and we added the ferromanganese in the cupola and part of the ferrosilicon in the form of lump, 50 per cent. ferrosilicon, and then added to the ladle, or in the spout rather, a mixture of 85 per cent. ferrosilicon and Grade F nickel shot, and we get tensile strengths up to 69,800 lb. We averaged better than 65,000 pounds.

R. MOLDENKE.—You notice that there was no graphite charged; therefore you did not introduce it.

H. BORNSTEIN.—We kept away from that.

R. MOLDENKE.—You see what the question of the degree of the original superheat means for any investigation you are going to make.

C. H. HERTY, JR.—We find temperature has such an important bearing, you simply realize you have another variable.

R. MOLDENKE.—Evidently it is the chief variable.

PROBLEMS IN DEFINING TERMS

C. H. HERTY, JR.—I am not so sure about that, but I think Mr. Capp has answered the question that I put to you when you asked me what was bad iron. I think that is the only way to tackle this thing. Of course, we must know what the stuff is going for, what it is good for, before we can begin to make iron.

There are three very distinct problems: (1) The problem of finding out what is meant by a bad casting—I have heard that about 300 times in the last year; (2) to work on the plant on castings you know are bad, after you get the definition, and (3) fundamental work to find out the effects of temperature, silicates, oxides, and so forth.

Obviously the fundamental facts and the finding of a bad casting can go on together because in fundamental work we are not trying to solve a particular problem. Regardless of whether the iron will be good, the plant work should follow the fundamental work absolutely, but if profitable plant work can be carried on along these lines with the fundamental work, that work can go along with Mr. Capp's remarks very nicely and follow his suggestions even better.

I strongly believe, from what I have heard in the last year, that the way to go at the thing is to have Dr. Gillett get together with the foundrymen and find out what is a bad casting and line up specifications to say that a casting is Grade A, B, C, D, E, and so on, and then start the fundamental work, because there is no use wasting time waiting for a bad casting to determine these things. At the same time I think very good work can be done out in the plant without having to wait for the fundamental work. Personally, I should prefer to do the fundamental work after the bad-iron specifications are set up.

J. A. CAPP.—There is only one objection to what Mr. Herty has said. Why do we want to define a bad casting? Let's define a good one instead. We are not trying to make bad castings; we are trying to make good ones. That is the abnormality; the good casting is what we are trying to make. If we have made a good casting, how do we know it is the best? If we have our measure of goodness—of course, it is a measure of badness on the negative side—we can tell whether we are making progress backward or forward. We can tell whether we are barely standing still.

When you come to what is intrinsic value in the casting, the report of what you have seen in Düsseldorf is intensely interesting, especially to the man who wants to make very strong castings. Some of us do not want to make strong castings. When you are trying to make little light things like covers or meter frames, strength is

almost a thing you do not want. What you want there is a casting that comes out of the sand whole and does not have much of a tendency to crack. Why should it crack? That is the first thing to find out. Was it molding practice or foundry practice in the sense of cupola work, or composition, or both?

Next, we want to have a casting that can readily be machined by ordinary equipment. If it is too hard, we will probably break the casting, unless we find very expensive ways of holding it to support it. The machine shop would like to find means to punch holes, if possible. Here the Düsseldorf report does not tell us a single thing of interest. I do not know the measure of goodness in that kind of casting.

I can cite a case of just how these things work. In one of our foundries we had a batch of pig iron with which they said they could not make good castings. The superintendent of one of the other foundries of the same company said he could make good castings out of it. He did, and the fight was on. It was a merry war. Just because it was so interesting, we did not call attention to the fact that the man who failed to make good castings was trying to make these little bits of thin things and the fellow who made the good castings was making a great, big, heavy, husky chunk, not too strong, but again, relatively easily machined. They had no common ground on which to start the fight. They were just fighting for the love of it.

R. MOLDENKE.—The great trouble is that we are emphasizing bad castings and good castings whereas we should emphasize good iron and bad iron. The quality of the casting is often a result of the foundry practice. If you put the gate in the wrong place, and thus not allow the mold to feed properly, you may get a casting full of shrinkages. We should emphasize the iron itself rather than the castings.

In one of the large foundries in the East they complained of bad pig iron. I investigated and found the following: They were melting under extreme economy in the cupola, holding the coke down. They took molten iron in a great big ladle. The temperature was right, and they poured a number of castings from each ladle. I noticed the metal in the pouring basins of the molds sucking down at first and then, as the iron cooled in the ladle, I noticed they froze flat, and toward the end they puffed up considerably. You could see the gas blowing out of the pouring basin. Why should that molten iron, while still liquid enough to pour, make bad castings full of blow holes, whereas when very hot the iron went all right?

There was something wrong with the iron, and yet it was satisfactory when the temperature was high enough. There are so many problems involved that it is very hard to develop the proper procedure to cover the situation.

A. MARKS, Waverley, Mass.—I think the foundrymen's difficulty is in the variety of work they have to deal with and also in the question as to who is to decide what is a good and a bad casting. To illustrate—I had control once of a large automobile works foundry. It was the practice to mill three sides of cylinders through a machine at one cut. I could put a mixture in to suit those cylinders and give a high rate of production, which would suit the production manager, but, putting the same cylinders into the final operation for the cylinder bores, which in that case was a roller pressure finish and not a grinding finish, there would be a tendency for the material, which would satisfy the speed requirements for milling, to open on the bore. If we changed over to grinding, that trouble would disappear. By reducing the outputs on the milling machines slightly, I could get a cylinder block that would satisfy the rolling finish for the bores and give perfect bores.

Now who is going to decide as to which iron we are going to have? That is the problem in brief of the metallurgist in any big concern.

I have had the pleasure of controlling some of the biggest foundries in the British Isles, where we ran every class of casting, from the smallest and lightest electrical work right up to the largest turbine practice. Before the war and during the war

we had to utilize any and every iron possible. In one case we were without pig iron at all, and I adopted the method which has been mentioned as being carried out in Germany, but, not wishing to introduce cement, I simply had boxes cast for the reception of the ferrosilicon and ferromanganese, boxes something like $\frac{3}{4}$ to $1\frac{1}{2}$ in. thick, according to the charge they were to be put into. I had them luted over with borings and then the top wedged down, the box being especially cast for the job.

Those charges were put in and run through a cupola and we got perfect iron.

But suppose we are casting a cylinder that may be 6 ft. long and 3 ft. 6 in. dia., and vary in thickness from the top end to the bottom end from $1\frac{1}{2}$ to $2\frac{1}{2}$ or $2\frac{1}{2}$ to $3\frac{1}{2}$ in. A very close iron would be used, a good iron; one can run it consistently and get 16 tons tensile strength day after day from those castings, the test bar being cast of the same diameter as the thickness of the middle of the cylinder—that is, from a $3\frac{1}{2}$ -in. cylinder I would have a $3\frac{1}{2}$ -in. test bar cast alongside it, the average thickness of the cylinder being 3 to $3\frac{1}{4}$ inches.

Those results would come out consistently and at our boring speeds the cylinders would bore consistently and give a consistent Brinell test for hardness, in addition to a consistent tensile strength day after day, but such iron would be useless for high-speed automobile work. It was possible to make those castings from various pig irons, but when an opportunity occurred for obtaining a blast furnace belonging to our own works simply for foundry iron, I laid down a definite specification for pig iron and we were supplied with two grades, one for open work and the other, a closer iron for running about No. 4, for close work.

There were all classes of castings made in those foundries and in one foundry alone, which had 400 molders, all the castings were run off that one grade of pig iron. The only adjustments that were made were the scrap returns and the addition in some cases to certain charges of a certain small quantity of steel, never more than 8 or 10 per cent.

That gives one big-scale experiment beyond an experimental state, an actual production state whereby through cooperation the blast furnace can be made to fit in with the foundry, but the metallurgist in the concern must have control of the production in regard to machining speeds and if the production manager is not satisfied with the speeds on one operation, and you know that increased speed on that operation is going to destroy the job in a subsequent operation, you must get a decision as to who is to control the product, if you are to do successful work.

Of course, where one is on one class of job and knows the tools from end to end, one can fix a definite mixture that will run right through the foundry, but only in a foundry producing one class of castings can that be done. Many of the troubles in the foundries are due to the fact that we cannot define, or do not attempt to define, a bad and a good casting. We start with good iron, and, for my part, any pig iron that is produced today can be made into a casting of some kind or other; in other words, every foundry iron produced is a good iron when used for a suitable class of castings. For instance, if I am running a light-grade casting with requirements for electrical work, light castings, I buy a high-grade phosphorus iron; but we must not ask anyone to put the same class of pig iron into a large turbine casting and get a satisfactory tensile job. We at once eliminate the blast furnace and buy another class of iron.

DEFINITE OBJECTIVE NECESSARY FOR RESEARCH

It is essential, first, if you are going to get out a program of research for the cast-iron industry, so as to cooperate with the blast-furnace people, that you shall have clearly in your mind what you want, what the machine man wants, before you can definitely make any progress; therefore I would suggest that we take the different grades of castings which foundrymen are familiar with and grade them with the

grades of thickness from automobile work up to turbine work, and so forth. The blast-furnace people can produce one, two, or three grades of pig iron and can easily turn out any grade of pig iron that you ask for, provided you are willing to put the thing on a big enough scale. You could run, say, in this country, three grades of pig iron which would give you the possibility of making any casting you wish. Those three grades of pig iron could be manufactured especially for foundry use and a specification could be made that would enable any manufacturer to produce those three grades of pig iron, and the various numbers could be used in the different mixtures.

You could, for instance, produce a number four iron continuously, but any competent metallurgist can take his various grades and mix them together so as to produce his daily requirements.

In regard to the good casting and the bad casting, we should first define what is good for a certain class of casting. What is good for an electrical casting is no good for an automobile casting and we know we could, therefore, get certain definitions and specifications laid down for each type of casting. Then we can make up from the definite mixtures definite pig irons, the mixtures to run through the cupolas to give the requirements for that particular grade.

Of course, anyone who is in the foundry continuously knows that he gets different metal according to whether it is a bed charge or charge run after five or six hours in the day. It differs in the temperature and carbon content, but those differences can be adjusted, just, for example, as I illustrated in the case of machining cylinder blocks, where it is necessary to close up the grain.

In another foundry with a machine shop attached, they may grind for the final finish and the metallurgist will not be troubled with that.

In addition to getting down to classes of foundry castings and different classes of pig iron for production of those castings, it should also be possible to lay down definite conditions under which the various mixtures or various irons could be used. For instance, if I run a mixture for a dry mold, there is not much use in attempting to put that mixture into a grain sand casting and, if I want to complain to a supplier of pig iron about bad iron, I could easily upset him by deliberately running a mixture of his iron into a quite unsuitable mold and calling him on the telephone next day to say, "Look what a rotten casting your iron produces!"

Any competent metallurgist with experience in the foundry can take these three different classes of pig iron and produce a good iron and a good casting with all the cooperation of his foremen in the matter of getting the correct mold.

There are, of course, troubles of the foundryman which can be related back to design, but I think, in order to make progress in research, I should make a list of what are bad castings, what are good castings, and the limitations of composition for the various grades of castings, and, finally, get down to the furnace people and get them to supply three definite brands of iron from which it would be possible to make up a mixture for any class of castings required.

R. MOLDENKE.—I am a little afraid that the American conditions will not fit in with the English conditions as described. We will never get back to grade numbers and fractures for our pig irons again.

A. MARKS.—All pig iron is purchased to specification but in the discussion it conveys rapidly to the listeners the kind of pig iron if one uses numbers, which are fairly definite in composition, for any particular brand of iron.

J. T. MACKENZIE, Birmingham, Ala.—The A. F. A. has wished off on my sub-committee the duty of formulating the problem and the test. We have done a good deal of work on that line. We have completed an investigation on the relation between true and apparent temperatures for foundry irons which I believe will give

considerable relief, bearing in mind that the freezing point of the iron and the temperature at which it comes out of the cupola determines the time required to pour and make a sound casting.

We have tried a number of mixtures, I think about 14 tests, varying from 2.60 carbon up to 3.80, and we find that the cooling rates are practically the same in all of the mixtures. A foundryman says that an iron is quick-setting because it freezes at a higher temperature, and the only reason for the one exception that exists, the oxidized iron, is that it is not freezing but evolving gas, which is worse than if it were freezing.

An iron with 3.77 carbon and 2.00 per cent. silicon is by no means a fluid iron yet is very soft. At 1250° or 1300° C. the graphite begins to come out so the practical fluidity of the iron is very low.

That brings to my mind another thing that Dr. Gillett is testing for us, the fluidity strip proposed by M. Curry at the Chicago meeting last year. We have decided on a few modifications of that, but it is in process of development.

Fluidity, which I believe is a function of the superheat above the freezing point, although we have still to prove that, would, of course, be dependent on the presence of graphite nuclei; if there were any considerable amount of nuclei present, it would be practically certain to reduce the fluidity.

Shrinkage trouble is very largely from pouring too hot, too high above the fusing point. It may be taken as axiomatic that if a cylinder of iron of eutectic composition is poured at the freezing point there would be no shrinkage. We must develop a test for liquid shrinkage as well as for "coolability."

In defining this problem, I believe we have nothing to do with what a man calls good or bad castings. We can say this iron gives this section certain physical properties, this section certain other physical properties, and so forth. We can say 40,000 lb. tensile strength in this section and it would mean that this man over here had no business with the iron, should not have it in the shop at all. The machinability and hardness may in some cases be related and in some cases may not, but all we can say is that this hardness on this 8-in. section is "so much." If he wants to be foolish enough to make $\frac{1}{2}$ in. sections with it, I do not see that this Committee needs to worry about that at all.

An amusing incident came to me a few months ago. A man buying coke asserted that the last car of coke was rotten, no good; he said, "I can't make a chill on the castings." This man was a friend of mine. He brought me two of the good castings made before he got the car of coke and three of the bad ones made afterwards. The two "good" ones had fully $\frac{1}{2}$ in. chill on them, and the three "bad" ones almost none. We analyzed the five and the castings that showed the good chill had 160 Si and the ones that showed no chill had 360 Si. In the end, we found that he had received a car of pig iron at the same time as the car of coke, but never thought of looking into the analysis of his pig.

TABULATION OF COMPLAINTS

H. W. GILLETT, Washington, D. C.—It seems to me that the discussion is getting down to brass tacks more than some of the previous ones. Heretofore there seemed to be an atmosphere of mystery about the fact that one particular lot from the blast furnace behaved differently from another, and so forth and so on, and we were so interested in talking about the mysteries that we did not get down to the facts. Today we are talking more about the facts.

It seems to me we are not interested in the properties of a good and bad casting at all—of a casting as such. It seems to me it is going at the thing wrong end to, because with a hundred different castings, it ought to be possible to analyze the causes for failures. You may not get them in CGS units. You will have to take something

more rough than that, but nevertheless you should be able to figure out what properties you are after.

Everyone who complains of the quality of pig iron should be required to put down in black and white exactly what he complains of, so that the troubles could be tabulated and grouped under a certain number of properties.

This business of ascribing all kinds of troubles in the foundry to the "metal" is not confined to pig iron alone. Many years ago when I was in the aluminum business, it was always the metal that was at fault. As a matter of fact, in the aluminum game at that time, 90 per cent. of the trouble ascribed to the metal came in the core room from the hard cores, because the metal cracks so readily. We ought to figure out all the tests anybody has any need for in determining the properties which are later reflected in a good or bad casting.

Making a list of the things that have come in so far—for instance, those mentioned today, and more fundamental ones—there are, first of all, temperature control before you can tell anything further and then there are two points in regard to molten metal. One of those was rate of solubility of graphite which comes into what you were talking about, the live or dead iron, and fluidity.

It is possible that the "fluidity strip," when the variables of the test are worked out, may give a pretty fairly direct measure of that. Incidentally, that is not so easy as it sounds. There are many variables and we have more respect for that project than when we took it on at first.

There also are the tensile properties and other ordinary physical properties; the machinability, which also is affected not only by the metallographic constituents but also by the sort of machining that is done, because turning, tapping, reaming and drilling are entirely different propositions. There ought to be some way of tabulating the properties of different compositions cast in different sections as to their machinability in the different operations.

There is pretty nearly 10 years' work on that before getting it down to quantitative terms. Then there is the propensity toward cracking and shrinkage which should be quantitatively ascertainable. There are the questions of blow holes and dissolved gas, and those of warpage and internal stress.

On some of these it is none too clear how one is going to make the test, but before we try to lay out any set of tests, it would be highly desirable to have listed all the tests we may need and some extra ones we think we may not need.

Some metallurgists reserve a certain number of specimens for "unknown tests," as the ancients used to have their altars and sacrifices to the "unknown gods."

So, the first thing is to continue along the lines of today's conference in segregating the properties we are after and methods of determining them, and when we know that we have the whole list, it will still be wise to reserve material for others we will think of after we are halfway through the job.

SOLUTION OF IRON OXIDE IN IRON

R. MOLDENKE.—This is a starting point, and it is good. What is being written up in the record this morning is good, and let me suggest another thing. My own experience indicates that the oxidation of material is one of the most important things in the question of fluidity. Can you not artificially make some iron in which you have dissolved iron oxide and see how it acts?

J. T. MACKENZIE.—Perhaps.

H. W. GILLETT.—According to Dr. Herty's work and to all physical chemistry theories of dessication, the *dissolved* iron oxide content of material so high in carbon as pig iron should be very small and very regular. The *suspended* iron-manganese silicate inclusions are another matter, and probably a more important one.

There are two ways of attacking the problem of oxygen and oxides analytically—one is the determination of total oxygen, with which we have been struggling at the Bureau of Standards for years, and on which the methods appear to be in fair working shape, with some remaining difficulties in the case of a high manganese content or the presence of alumina, on which we are still working. The method has been applied to coke and charcoal irons and the results published in the *Transactions* of the American Foundrymen's Association. While the method is essential if "residue" methods do not recover all the oxygen so that calculations as to type of oxides present require a knowledge of total oxygen, it does not seem, alone, to promise much light on pig-iron quality.

The other line of attack, separating the oxides by "residue" methods, is being studied by Herty, and we are doing some work along those lines too, chiefly on steel. The large amount of graphite in the residues mixed with the very small amount of oxides makes the residue methods none too easy of application. Much tedious and precise work on analytical methods has still to be done before wholly reliable results can be expected.

CLASSIFICATION OF IRONS

J. W. BOLTON, Cincinnati, Ohio.—It is very encouraging indeed to note that the trend in the discussion is toward more fundamental investigations. We have had a number of things given to us that are bound to bear fruit, but it seems to me that perhaps the first or primary thing that should be done has not been given the prominence it should. We have spoken this afternoon of gray iron. There is no such thing as gray iron, to which you can apply all these fundamental tests of engineering properties and get any intelligible results. The first thing that must be done is to classify the gray irons into groups. They may have to be arbitrary groups, but you are working with a series of alloys, not a given alloy. A non-ferrous man would think it the height of indiscretion to conduct an investigation on bronzes. He defines his bronzes, working on 88-10-2, 85-5-5-5, and so forth. On cast iron we are discussing a whole field of alloys, which may range from a possibility of around 2.20 total carbon in commercial irons, close to 4 per cent. total carbon. The first thing to line up is the different groups of cast iron and along that line the first thing you probably would have to do is to line them up according to composition. For example, we could group the irons into a number of carbon classes—say, divide the carbons every 25 or 50 points, feeling that cast iron is essentially an iron-carbon alloy and the two important things that influence the properties of these carbons, the big things in composition, are silicon and total carbon.

We could divide them into carbon groups and subdivide into silicon groups, and even further, according to manganese and sulfur, etc. Then we would have a classification according to composition and according to thermal history.

The shop man does that in a qualitative manner by his so-called section size. As has been brought out in the discussion this afternoon, that is only one of many factors brought into it. There are many steps, including the reduction in the blast furnace to the rate of pouring and the cooling conditions in the mold. If we combine the classification of irons according to composition, subgraded according to thermal history, then go after the engineering properties of which Dr. Gillett names a number and we lined up some 65, and take each of the groups, there would be 40 or 50 in composition, and within that a number of thermal groups. You could take each one and whip it out, and have something to get hold of with all these variables. It is a very complex subject, and the further you get into it, the more complex it becomes.

You could have iron A, B, C, D, cast under X, Y, Z, and by the time you have the fundamentals, we would be in a more intelligent position to go after these more mysterious alchemistic properties of iron.

COKE IRON AND CHARCOAL IRON

R. FRANCHOT, Washington, D. C.—When this problem of pig iron quality gets back to the blast furnace, which I assume that it will very soon now, it seems that we will be faced with one very interesting, outstanding fact and that is the difference between coke iron and charcoal iron. The problem of pig-iron quality appears to be intimately related to that of blast-furnace fuel economy.

Last year in connection with Dr. Moldenke's paper on foundry iron it was brought out that it takes less carbon in the form of charcoal to make iron than it does as coke. When it is considered that not only is substantially less carbon but also as a rule much less blast heat used in charcoal practice, the difference in fuel economy—the wastefulness of coke—becomes very striking. This difference carries more than a suggestion that the factors that determine fuel economy, coke consumption—in short, the burden ratio—may have much to do also with the quality of the product.

There is thus to be seen an attractive possibility of solving by research two problems at once—fuel economy and iron quality. We are faced with the fact that not only is charcoal iron better for many purposes than coke iron but also, in terms of carbon consumption, it is cheaper. If a way could be found to make coke practice approach nearer to charcoal practice in heat economy, the chances are, as a matter of pure empiricism, that we could make not only cheaper iron but better iron.

Why, then, is it that so much more heat is required to smelt the same ore with coke than with charcoal? The answer usually given is based on the differences between coke and charcoal in ash content and in sulfur content. There can be no doubt that these facts have to be considered in seeking an answer to the question. Having much more sulfur to contend with, the coke furnace usually has to produce more slag, and a more basic slag as well. Consequently it has to be run at a higher hearth temperature than the charcoal furnace. These conditions were clearly presented by Mr. Joseph three years ago.¹ At that time it was brought out that sulfur, an element constituting something like 0.15 per cent. of all the materials going through the furnace, is probably to be held indirectly responsible for an average difference of 20 or 25 per cent. in the fuel consumption per unit of iron. To this indirect effect of the sulfur is to be added a difference of 100 per cent. in blast heat, as the blast in coke furnaces often is twice as hot as with charcoal. In an extreme case these differences may be more marked even with slag ratios favoring coke: an Austrian charcoal furnace, described by Lowthian Bell,² having a working volume of 1200 cu. ft. with a 3-ft. hearth, made 20 tons of iron a day with a 60 per cent. slag ratio at a consumption of 1400 lb. of 85 per cent. charcoal per ton and a blast heat of 400° F. In specific efficiency, that is, in smelting work done per unit of carbon plus blast heat, this furnace was 36 per cent. better than the best coke practice using 1200° heat. The hearth work in such practice, as measured by the heat nominally available at 2732° F., is 414 B.t.u. per pound pig, which compares with 1145 B.t.u. in the South Chicago practice as described by Mathesius,³ where the slag ratio was 45.5 per cent. If a temperature difference of 180° F. (100° C.) be assumed, the heat available to the hearth in the charcoal furnace becomes 538 B.t.u. per pound pig. To explain this doubling of the hearth heat requirement in coke practice as compared with charcoal, I have offered the hypothesis⁴ that it is related to the known increase, with heat and basicity, of the chemical activity of the air nitrogen as evidenced in various ways; in particular by the presence of alkali cyanide in substantial amounts

¹ T. L. Joseph: Effect of Sulfur on Blast-furnace Process. *Trans.* (1925) 71, 453.

² I. L. Bell: Chemical Phenomena of Iron Smelting, Sec. 43. London, 1872. Routledge.

³ W. Mathesius: High Blast Heats in Mesaba Practice. *Trans.* (1915) 51, 794.

⁴ R. Franchot: The Theory of the Blast Furnace. Amer. Iron and Steel Inst. Yearbook (1927) 150.

in the hearth and bosh. If there is another available explanation of the phenomenon it would be interesting to have it presented.

To cover in detail all the wide differences between coke and charcoal economy would require an excursion into the fundamental theory of the blast furnace. For such an excursion time is lacking.

The blast-furnace theory as prevailing today presents a most interesting complex. Sir Lowthian Bell in 1872 sponsored the theory that the coke ratio is determined by the requirement of a great excess of CO in order to reduce the ore to metal. About 1904 Johnson seems to have spiked this theory quite conclusively when he showed the thermal significance of blast heat and pointed out that the excess of CO instead of being a cause is an effect of the large amount of coke required to maintain the hearth heat. However, being at a loss to explain the necessity for the goodly amount of hearth heat that is used in coke practice, Johnson practically accepted Bell's theory when he arbitrarily assumed that a substantial part of the iron reduction devolves upon the hearth. As a result, the ideas prevailing today are a complex of Bell's and Johnson's. That the coke ratio is determined in the hearth is well understood in practice and yet in nearly every textbook will be found a statement that the reduction equilibrium is the underlying limiting factor. Bell had a comfortable conviction that his furnaces approached theoretical perfection when his top gas showed a 33 per cent. CO₂ ratio. Today, with a modification up to 38 per cent., Bell's conviction seems to be quite generally shared in spite of a CO₂ ratio in charcoal practice running well over 50 per cent. The close relation between theory and practice is proved, if proof were needed, by the fact that today's fuel economy is on the average no better than Bell's. Prevailing theory and standardized metallurgical practice during 50 years have apparently condemned the coke furnace forever to be more gas producer than iron smelter, and the trend of the industry is increasingly toward a primary use of the furnace as gas producer for the steel plant with pig iron as a by-product. If the gas were an efficient fuel this practice would not be as uneconomical as it actually is.

It is plainly to be seen that, in the interest of lower costs and of better iron as well, the furnace needs primarily some destructive criticism of prevailing ideas, to be followed by constructive theoretical treatment. There probably has seldom been a more promising opportunity for constructive research than is presented today by the question: What is the distribution of the hearth heat? Or more particularly, why is the metallurgy of charcoal so much better than that of coke?

CONCLUSION

H. BORNSTEIN.—I feel that we should take some action, and if it is in order, I should like to make a motion that this problem be turned over to the subcommittee on research of the A. F. A. in cooperation with Dr. Gillett of the Bureau of Standards, and also Dr. Herty, of the Bureau of Mines, to submit recommendations, if they are ready to do so, at the Philadelphia meeting of the A. F. A. in May, and also include in that Mr. Sweetser, of the blast-furnace people, to cooperate.

The motion was seconded by W. Rother, of Buffalo, N. Y.

T. C. DAVIS: Is that not rather contrary to the resolution previously presented? You should find out what you want before going further in the matter.

H. BORNSTEIN. We cannot do that at a meeting of this sort. It would have to last from now until March to determine what things we want, but a small committee of three, four, five, or six could get together and study the thing, and perhaps by next May they might be able to offer the beginning of a definite program.

J. A. CAPP.—It seems to me that the only sensible way to interpret the motion which has been made is that this committee is to present the program as it was provided in the statement of principles. They are not in conflict. One follows the other.

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